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Aerobic oxidation of ethane to acetic acid catalyzed by *N*,*N*′-dihydroxypyromellitimide combined with Co species

Akihiro Shibamoto, Satoshi Sakaguchi and Yasutaka Ishii*

Department of Applied Chemistry, Faculty of Engineering and High Technology Research Center, Kansai University, Suita, Osaka 564-8680, Japan

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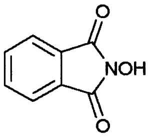
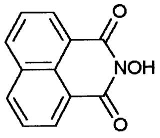
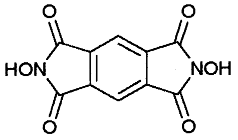
Abstract—Aerobic oxidation of ethane to acetic acid was successfully performed through a catalytic radical process using *N*,*N*′-dihydroxypyromellitimide (NDHPI) combined with a Co(II) salt in acetonitrile or propionic acid. The turnover number of NDHPI reached 9.5 in acetonitrile and 15.3 in propionic acid. © 2002 Elsevier Science Ltd. All rights reserved.

Methane and ethane are the main components of natural gas which has been long used worldwide as a clean fuel. Since ethane comprises 5–10% of the natural gas, a vast amount of ethane is formed with production of methane. Like methane, ethane is also a most unreactive class of hydrocarbons which are very difficult to be converted into useful organic chemicals. If a new methodology for converting ethane efficiently to useful oxygen-containing compounds like ethanol and acetic acid is developed, it would vastly contribute to the efficient use of feedstock. There have been several works for the conversion of ethane to acetic acid under heterogeneous catalysts using mixed metal oxides,[1] but the transformation of ethane under homogeneous conditions is rarely studied.[2] Therefore, the direct catalytic conversion of ethane to oxygenates is an enormous challenge in oxidation chemistry as well as industrial chemistry. Previously, Sen et al. reported liquid-phase oxidation of ethane to acetic acid and formic acid by Pd/C with H_2O_2 generated in situ from H_2, arising from a metal-catalyzed water gas shift reaction with CO and water, and O_2.[3] Fujiwara et al. showed that ethane can be converted into *N*,*N*-dimethylpropylamine by the reaction with *N*,*N*-trimethylamine *N*-oxide in using $Cu(OAc)_2$ as the catalyst.[4] Ethane oxidation with H_2O_2 catalyzed homogeneously by V-containing polyphosphomolybdates has been carried out by Shul'pin et al.[5] In previous papers, we have reported that alkanes like cyclohexane and toluene can be oxidized with molecular oxygen by the use of *N*-hydroxyphthalimide (NHPI) which serves as a carbon radical-producing catalyst (CRPC) from alkanes.[6] In this paper, we would like to report the oxidation of ethane to acetic acid with air using CRPC like NHPI and its analogues.


NHPI


NHNI


NDHPI

In order to confirm suitable catalysts in this transformation, ethane was reacted under various conditions using NHPI and its analogues as catalysts (Table 1).

A typical reaction was examined as follows: The reaction was carried out in a 50-mL teflon-coated autoclave. To acetonitrile (5 mL) was added NHPI (100 μmol) and $Co(OAc)_2 \cdot 4H_2O$ (30 μmol), and then ethane (20 atm, ca. 70 mmol) and air (20 atm) were charged. The mixture was stirred at 150°C for 15 h. After the reaction, products were subjected to GC and GC–MS analyses.

Among the catalysts examined, *N*,*N*-dihydroxypyromellitimide (NDHPI) was found to be the best catalyst. For instance, when a mixture of ethane (20 atm) and air (20 atm) in acetonitrile (5 mL) was allowed to react in the presence of NDHPI (100 μmol) and $Co(OAc)_2$ (30 μmol) at 150°C for 15 h (standard conditions), 830 μmol of acetic acid was obtained and the turnover number (TON) of NDHPI reached 8.3 (Run 5). It is noted that other products such as ethanol or acetaldehyde were not detected at all under these reac-

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Keywords: oxidation; ethane; *N*-hydroxyphthalimide; catalysis.

* Corresponding author. Tel.: +81-6-6368-0793; fax: +81-6339-4026; e-mail: ishii@ipcku.kansai-u.ac.jp

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Table 1. Aerobic oxidation of ethane (**1**) to acetic acid (**2**) by NHPI analogues[a]

Run	Catalyst	Solv. (mL)	$Co(OAc)_2$ (μmol)	Yield[b] (μmol)	TON
1	NHPI	CH_3CN (5)	20	530	2.7
2	NHPI	CH_3CN (10)	20	612	3.1
3	NHPI	PhCN (5)	10	150	0.75
4	NHNI	CH_3CN (5)	40	200	1.0
5	NDHPI	CH_3CN (5)	30	830	8.3
6	NDHPI	CH_3CN (7)	25	570	5.7
7	–	CH_3CN (5)	30	<5	–

[a] The reaction was carried out in the presence of catalyst (200 μmol for NHPI and NHNI and 100 μmol for NDHPI) at 150°C for 15 h.
[b] GC yield.

tion conditions. In the oxidation of ethane using NHPI as a catalyst under these conditions, the amount of NHPI used was twice that of DHPI, but the yield of acetic acid and the TON of the catalyst were 530 and 2.7 μmol, respectively (Run 1). Similarly, *N*-hydroxynaphthalimide (NHNI) was less active to form 200 μmol of acetic acid. Although the oxidation was examined in various solvents like benzonitrile, nitromethane, benzene, and trifluorotoluene, the solvents other than acetonitrile gave in unsatisfactory results. No oxidation was induced by $Co(OAc)_2$ alone without a radical-producing catalyst like NHPI (Run 7).

On the basis of these results, the oxidation of ethane catalyzed by NDHPI was carried out by varying the conditions (Table 2).

The yield of acetic acid was found to slightly increase with rise of the reaction temperature over 150°C (Runs 1 and 2). The oxidation took place to some extent even at 120°C, but the yield of acetic acid became very low (Run 5). Although the reaction under lower ethane pressure than 20 atm resulted in decrease of acetic acid, no large effect of air pressures was observed (Runs 6–8). We next examined the effect of a Co species in the oxidation of ethane under the standard conditions by using the NDHPI catalyst. Divalent Co species were found to be better additives than a trivalent Co one (Runs 9 to 11). Among the divalent cobalt species examined, $CoCl_2$ and $Co(NO_3)_2$ were found to be good additives to the NDHPI catalyst leading to 946 or 892 μmol of acetic acid, respectively (Runs 9 and 10).

It is known that acetonitrile and benzonitrile are hydrolyzed in basic or acidic medium to yield the corresponding carboxylic acids. Since the present ethane oxidation is carried out in acetonitrile which is liable to lead to acetic acid in the cource of the reaction, the ethane oxidation was examined in deuterated acetonitrile, CD_3CN, under the influence of NDHPI and $CoCl_2$ (Eq. (1))

$$\underset{20\ \text{atm}}{C_2H_6} + \underset{20\ \text{atm}}{\text{air}} \xrightarrow[\substack{CD_3CN\ (5\ \text{mL})\\ 150\ ^\circ C,\ 15\ \text{h}}]{\substack{\text{NDHPI}\ (100\ \mu\text{mol})\\ CoCl_2\ (30\ \mu\text{mol})}} \underset{\left(\substack{CD_3COOH\\ \text{not detect}}\right)}{CH_3COOH} \qquad (1)$$

The GC–MS spectrum of the reactant indicated the formation of CH_3COOH having $m/e = 60$ formed by the oxidation of ethane and no evidence of the formation of CD_3COOH arising from hydrolysis of CD_3CN. This observation suggests that the acetic acid is derived from ethane.

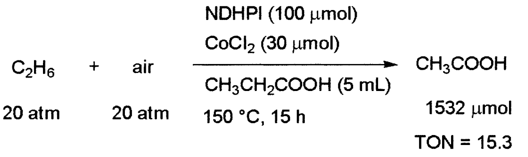
In a previous paper, it was reported that acetic acid is a good solvent in the NHPI-catalyzed oxidation of cyclohexane and toluene with O_2. Since the present ethane oxidation produced acetic acid as the sole product, it is difficult to estimate the amount of the resulting acetic acid by the oxidation of ethane using acetic acid as the solvent. Thus, the oxidation was examined in a homologue of the acetic acid, propionic acid, under standard conditions (Eq. (2)). It was found

Table 2. Aerobic oxidation of ethane (**1**) to acetic acid (**2**) by NDHPI under various conditions[a]

Run	Temp. (°C)	Co species	Ethane (atm)	Air (atm)	Yield (μmol)	TON
1	170	$Co(OAc)_2$	20	20	888	8.9
2	160	$Co(OAc)_2$	20	20	845	8.5
3	150	$Co(OAc)_2$	20	20	829	8.3
4	140	$Co(OAc)_2$	20	20	470	4.7
5	120	$Co(OAc)_2$	20	20	135	1.4
6	150	$Co(OAc)_2$	30	10	709	7.1
7	150	$Co(OAc)_2$	10	10	380	3.8
8	150	$Co(OAc)_2$	10	30	309	3.1
9	150	$CoCl_2$	20	20	946	9.5
10	150	$Co(NO_3)_2$	20	20	892	8.9
11	150	$Co(acac)_3$	20	20	338	3.4

[a] A mixture of ethane (**1**) and air was reacted using NDHPI (100 μmol) and Co species (30 μmol) at 120–170°C for 15 h.

that the oxidation of ethane in the propionic acid produced acetic acid in good yield (1532 μmol) and TON (15.3). It is known that propionic acid is aerobically oxidized to acetic acid.[7] Therefore, we examined the control experiment. When propionic acid was allowed to react in the presence of DHPI and $CoCl_2$ under pressure of air/N_2 (20/20 atm), acetic acid was obtained in 135 μmol. This fact shows that a very small amount of propionic acid is converted into acetic acid. These results show that aliphatic carboxylic acids like acetic acid and propionic acid are also good solvents to convert light alkanes into the corresponding carboxylic acids.



$$\underset{20\ \text{atm}}{C_2H_6} + \underset{20\ \text{atm}}{\text{air}} \xrightarrow[\substack{CH_3CH_2COOH\ (5\ \text{mL}) \\ 150\ °\text{C},\ 15\ \text{h}}]{\substack{\text{NDHPI}\ (100\ \mu\text{mol}) \\ CoCl_2\ (30\ \mu\text{mol})}} \underset{\substack{1532\ \mu\text{mol} \\ \text{TON} = 15.3}}{CH_3COOH} \quad (2)$$

In conclusion, carbon radical-producing catalysts (CRPC) like NHPI and NDHPI were found to be efficient for the conversion of ethane to acetic acid under relatively mild conditions. This method can be expected as an alternative methodology of alkane oxidation with air, although further improvement of the catalyst is needed to run the reaction in practical scale.

Acknowledgements

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