CLEAN SYNTHESIS OF ADIPIC ACID BY DIRECT OXIDATION OF CYCLOHEXENE IN THE ABSENCE OF PHASE TRANSFER AGENTS

Heng Jiang*, Hong Gong, Zhonghua Yang, Xiaotong Zhang and Zhaolin Sun

Department of Material Science, Fushun Petroleum Institute, Fushun 113001, China
E-mail: hjiang78@hotmail.com

Received July 9, 2001
In revised form November 6, 2001
Accepted November 26, 2001

Abstract

In the absence of phase-transfer agents, the ligand effects are studied for the clean synthesis of adipic acid by direct oxidation of cyclohexene catalyzed by Na₂WO₄·2H₂O with 30% hydrogen peroxide. In most cases, the isolated yield of the target product adipic acid is high if the ligand acidity is strong. Although the acidity of some phenolic ligands, L(+)-ascorbic acid and 8-quinolinol is weak, the isolated yield of adipic acid is still high. It is demonstrated that the acid and coordination effect of the ligand play the same important role in the Na₂WO₄·2H₂O catalyzed oxidation of cyclohexene to adipic acid with 30% hydrogen peroxide. Kinetic investigations show that the hydrolysis of cyclohexene oxide to 1,2-cyclohexandiol is the critical step and the acidity of reaction system is important.

Keywords: Adipic acid, cyclohexene, catalytic oxidation, acidic ligand

INTRODUCTION

Adipic acid is an important intermediate utilized in the production of nylon-6,6. The usual industrial synthesis of this compound involves nitric acid oxidation [1]. However, N₂O emission from nylon-6,6 production accounts for 5 to 8% of the total amount released by man [2].
For the catalytic oxidation of cyclohexene to adipic acid, earlier workers used 35% H$_2$O$_2$ and ($N$-n-C$_{16}$H$_{33}$pyridinum)$_3$(PW$_{12}$O$_{40}$) or H$_2$WO$_4$ in tert-butyl alcohol [3] or in other patented procedures either 40% H$_2$O$_2$ and [CH$_3$(n-C$_8$H$_{17}$)$_3$N]$_3$PO$_4$[W(O)(O$_2$)$_2$]$_4$ in 1,2-dichloroethane [4] or 60% H$_2$O$_2$ and H$_2$WO$_4$ [5]. The byproducts were glutaric acid, peroxy acids, and 1,2-cyclohexanediol. With 35% H$_2$O$_2$ and a H$_2$WO$_4$ catalyst, only a trace amount of adipic acid was obtained [6].

Oxidation with aqueous H$_2$O$_2$ as the oxidant is appreciated because water is the sole expected side product [7]. In 1998, R. Noyori et al. described a very efficient cleavage of olefins to carboxylic acids by Na$_2$WO$_4$·2H$_2$O/[CH$_3$(n-C$_8$H$_{17}$)$_3$N]HSO$_4$ with 30% hydrogen peroxide at 75-90°C in ca. 8 h [8]. As no organic solvent and halide are involved, this economical method may be of special industrial interest as an example of so-called „green chemistry“. Deng et al. employed peroxytungstate complexes as catalysts for the direct oxidation of cyclohexene with 30% aqueous hydrogen peroxide [9,10]. Considering that the synthesis of [CH$_3$(n-C$_8$H$_{17}$)$_3$N]HSO$_4$ is complicated and tedious [11], we have reported the method of replacing [CH$_3$(n-C$_8$H$_{17}$)$_3$N]HSO$_4$ with the simple sulfate and hydrochloride of a higher primary or tertiary amine [12]. Our further research showed that the acidity of ligand plays a very important role for the Na$_2$WO$_4$·2H$_2$O catalyzed oxidation of cyclohexene with 30% aqueous hydrogen peroxide, and there is no need of phase-transfer agents.

EXPERIMENTAL

Materials and reagents

Analytical grade 30% aqueous hydrogen peroxide was purchased from Shanghai Yuanda Peroxide, Inc., and used as received. Chemically pure cyclohexene was obtained from Shanghai Chemical Reagent No.1 Factory and was distilled under Nitrogen before use. Analytical grade sodium tungstate dihydrate was purchased from Shenyang No.1 Chemical Reagents Factory. The others reagents are all analytical grade.

Catalytic oxidation

A 150 mL flask equipped with a magnetic stirring bar and a reflux condenser was charged with 0.825 g (2.5 mmol) of Na$_2$WO$_4$·2H$_2$O, 2.5 mmol of ligand, and 44.5 mL (440 mmol) of 30% aqueous H$_2$O$_2$. The mixture was vigorously stirred at room temperature for 15 min and then 10.5 mL (100 mmol) of cyclohexene was added. The biphasic mixture was then heated and refluxed for