Asian Journal of Chemistry; Vol. 25, No. 11 (2013), 6008-6010

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14230

Synthesis of Adipic Acid Oxidized by H_2O_2-Silicotungstic Acid Under Ultrasonication

ZHI-PING LIN* and LI WAN

Department of Biology and Chemistry, Baoding University, Baoding 071000, P.R. China

*Corresponding author: E-mail: linzhiping888999@163.com

(*Received*: 25 June 2012; *Accepted*: 24 April 2013) AJC-13389

A green synthesis of adipic acid from cyclohexene oxidized by H_2O_2-silicotungstic acid was carried out in 92 % yields at 30 ºC within 4 h under ultrasound irradiation.

Key Words: Adipic acid, H_2O_2-silicotungstic acid, Synthesis, Ultrasound irradiation.

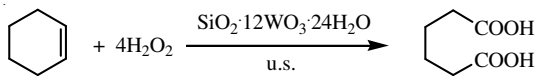
INTRODUCTION

Adipic acid is of great importance commercially in that it is used as a starting reagent in the preparation of nylon-66, a polymetric material used in carpet fibres, tyre reinforcement, automobile parts, clothing and many other everyday life applications[1,2].

Using nitric acid, potassium permanganate, molecular oxygen, ozone, sodium hypochlorite as the oxidizing agent, the oxidation of cyclohexene, cyclohexanol, cyclohexanone or a mixture of them or electro-oxidation of cyclohexanol gave adipic acid in many reports[3]. Hydrogen peroxide as a safe, gentle, clean, low cost and readily available oxidant, can replace traditional high-polluting oxidants in organic synthesis. A one-pot synthesis of adipic acid was reported from cyclohexene and *tert*-butyl hydroperoxide yielded in 80 % under mild conditions (353 K, 24 h) with new bifunctional Ti-AlSBA mesostructured catalysts[4]. The oxotungsten-silica mesoporous structure (WSBA-15) catalyst can be recycled-without any loss of activity-for the direct oxidation (30 % H_2O_2) of cyclohexene to adipic acid (55 % yield) under organic solvent-free conditions[5]. Cyclohexene, cyclohexanol, cyclohexanone and 1,2-cyclohexanediol oxidized by 30 % hydrogen peroxide to adipic acid in 15-83 % yields within 20 h at 90 ºC using surfactant-type peroxotungstates and peroxomolybdates as catalyst without organic solvent and phase-transfer catalyst[6]. Ren *et al.*[7] reported the synthesis of adipic acid from cyclohexene and hydrogen peroxide catalyzed by complexes derived from heteropoly acid and glycine in higher yield of 95 % at 90 ºC within 12 h. Blach *et al.*[8] proposed a recyclable and environmentally friendly process for the oxidation of cyclohexene to adipic acid in yield 56-97 % by hydrogen peroxide and sodium tungstate at 70 ºC for 18 h in microemulsions. Under the condition of organic solvent and phase-transfer catalyst all free, $Na_2WO_4{\cdot}2H_2O$, sulphuric acid and 30 % H_2O_2 were stirred 0.5 h to prepare *in situ* the peroxy tungstate catalyst, then cyclohexene was added and the system was heated to reflux for 6 h at 80-95 ºC, a 94.5 % yield of adipic acid was obtained[9].

Heteropolyacids are found to act as outstanding catalysts in electrophilic transformations[10]. Silicotungstic acid is a solid heteropolyacid, which has been used for the synthesis of trioxanes[11], alkylation of benzene with olefins[12], production of acrolein from glycerol[13], cyclodehydration of 1,4-butanediol to tetrahydrofuran[14], *bis*(indol-3-yl)pyrazolyl methanes[15] and *bis*(indol-3-yl)methanes[16]. These results have shown that silicotungstic acid has high catalytic activity and good stability and is an environmentally friendly catalyst.

Ultrasound has increasingly been used in organic synthesis in the last three decades. A large number of organic reactions can be carried out in higher yields, shorter reaction time or milder conditions under ultrasound irradiation[17]. In this paper we wish to report a green and efficient procedure for the synthesis of adipic acid with the oxidized by hydrogen peroxide from cyclohexene under ultrasound irradiation at room temperature (**Scheme-I**).



Scheme-I: Synthesis of adipic acid

EXPERIMENTAL

Liquid substrates were distilled prior to use. Melting points were uncorrected. Sonication was performed in Shanghai BUG40-06 or BUG25-06 ultrasonic cleaner (with a frequency

of 25, 40 and 59 kHz and a nominal power 250 W; Shanghai Kudos Ultrasonic Instrument Co., Ltd.). The reaction flask was located in the maximum energy area in the cleaner, where the surface of reactants is slightly lower than the level of the water. The reaction temperature was controlled by addition or removal of water from ultrasonic bath.

General procedure for the preparation of adipic acid: A 50 mL round flask was charged with cyclohexene (2 mmol), silicotungstic acid (0.04 mmol) and 30 % H_2O_2 (10 mmol) in one portion. The reaction flask was located in the cleaner bath, where the surface of reactants was slightly lower than the level of the water. The mixture was irradiated 4 h (the reaction was monitored by TLC). The reaction products were isolated by filtration from the reaction mixture. Then the solvent was poured into crushed ice. The precipitate was separated by filtration, washed with water and crystallized from water to obtain the adipic acid 265 mg, 92 %, m.p. 152-153 ºC.

RESULTS AND DISCUSSION

To optimize the reaction conditions, a series of experiments at varying amount of silicotungstic acid were carried out. As shown in Table-1, the adipic acid obtained the higest yield (92 %) at a molar ratio of cyclohexene: silicotungstic acid of 1:0.02. The yields decreased when changing this molar ratio. It indicates that the molar ratio had a significant effect on this reaction.

TABLE-1
EFFECTS OF THE AMOUNT OF SILICOTUNGSTIC ACID ON THE OXIDATION OF CYCLOHEXENE TO ADIPIC ACID UNDER ULTRASOUND IRRADIATION*

Amount of silicotungstic acid (mmol)	0.02	0.03	0.04	0.05	0.06
Yield (%)	66	85	92	90	89

*Ultrasound frequency: 25 kHz; 30 %, H_2O_2: 10 mmol; reaction time: 4 h; reaction temperature: 30 ºC.

The effect of amount of H_2O_2 on reaction was investigated. When the amount of H_2O_2 was 8, 9 and 10 mmol, the yield was 65, 88 and 92 %, respectively. No improvement was observed while increasing the amount of H_2O_2 (Table-2).

TABLE-2
EFFECTS OF THE AMOUNT OF H_2O_2 ON THE OXIDATION OF CYCLOHEXENE TO ADIPIC ACID UNDER ULTRASOUND IRRADIATION*

Amount of H_2O_2 (mmol)	8	9	10	11	12
Yield (%)	65	88	92	88	79

*Ultrasound frequency: 25 kHz; silicotungstic acid: 0.04 mmol; reaction time: 4 h; reaction temperature: 30 ºC.

Under stirring condition, the adipic acid was obtained in only 33 % yield within 4 h in the absence of ultrasound (Table-3). While under ultrasound of 59, 40 and 25 kHz, the yield improved to70, 79 and 92 %, respectively in the same time. It is apparent that the lower frequency of ultrasound can accelerate the oxidation.

The effect of reaction time was shown in Table-4, no improvement was found in a prolonged reaction time. The reason may be that the prolonged reaction time would cause many other by-products within the reaction system.

TABLE-3
EFFECT OF ULTRASOUND FREQUENCY ON THE OXIDATION OF CYCLOHEXENE TO ADIPIC ACID*

Ultrasound frequency (kHz)	25	40	59	Stiring
Yield (%)	92	79	70	33

*30 % H_2O_2: 10 mmol; silicotungstic acid: 0.04 mmol; reaction time: 4 h; reaction temperature: 30 ºC.

TABLE-4
EFFECT OF REACTION TIME ON THE OXIDATION OF CYCLOHEXENE TO ADIPIC ACID UNDER ULTRASOUND IRRADIATION*

Reaction time (h)	3.0	4.0	5.0	6.0
Yield (%)	84	92	83	78

*Ultrasound frequency: 25 kHz; 30 % H_2O_2: 10 mmol; silicotungstic acid: 0.04 mmol; reaction temperature: 30 ºC.

As shown in Table-5, when the reaction was carried out at 30 ºC, the adipic acid was obtain in 92 % yield, while when the temperature was 25, 35 and 40 ºC, the yield was 87, 86 and 83 %, respectively. This may be that the lower reaction temperature caused the lower reactivity, but the higher reaction temperature would cause other complex oxidation by-products and difficult workup procedures.

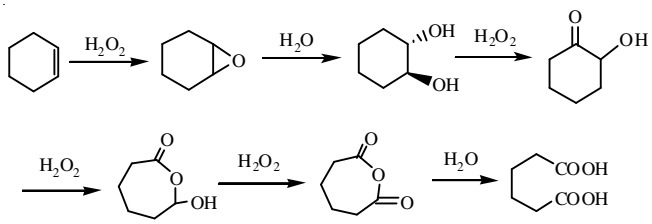
TABLE-5
EFFECT OF REACTION TEMPERATURE ON THE OXIDATION OF CYCLOHEXENE TO ADIPIC ACID UNDER ULTRASOUND IRRADIATION*

Reaction temperature (ºC)	25	30	35	40
Yield (%)	87	92	86	83

*Ultrasound frequency: 25 kHz; 30 % H_2O_2: 10 mmol; silicotungstic acid: 0.04 mmol; reaction time: 4 h.

As the data reported in literature[4-9], cyclohexene oxidized by 30 % H_2O_2 to adipic acid in 55-94.5 % yield at 70-95 ºC within 6-20 h. While under ultrasound and hydrogen peroxide-silicotungstic acid-oxidation, the adipic acid was given in 92 % yields at 30 ºC within 4 h. The most important was the useless of the phase transfer catalyst in ultrasonic system.

The reaction seems to occur via a classic multi-step conversion including three kinds of oxidation pathway (olefin epoxidation, oxidation of diol and Baeyer-Villiger oxidation) and the hydrolysis process[1].



Scheme-II: Synthesis of adipic acid *via* the oxidized by hydrogen peroxide

Conclusion

Ultrasound irradiation can accelerate the oxidation of cyclohexene, high adipic acid yields, shorten reaction time, optimize the reaction conditions and simplify operation procedures.

ACKNOWLEDGEMENTS

The authors thank the Natural Science Foundation of Hebei Education Department (Z2010101) and Natural Science Foundation of Baoding University (2009002), China for financial support.

REFERENCES

1. K. Sato, M. Aoki and R. Noyori, *Science*, **281**, 1646 (1998).
2. (a) Z.H. Liang, Y.Q. Cui and H.Y. Sun, *Electrochemistry*, **14**, 40 (2008). (b) D. Bonnet, T. Ireland, E. Fache and J.P. Sinomato, *Green Chem*., **8**, 556 (2006).
3. G. Rothenberg and Y. Sasson, *Tetrahedron*, **52**, 13641 (1996).
4. (a) G. Lapisardi, F. Chiker, F. Launay, J.P. Nogier and J.L. Bonardet, *Catal. Commun*., **5**, 277 (2004); (b) G. Lapisardi, F. Chiker, F. Launay, J.P. Nogier and J.L. Bonardet, *Micropor. Mesopor. Mater.*, **78**, 289 (2005).
5. C.Y. Cheng, K.J. Lin, M.R. Prasad, S.J. Fu, S.Y. Chang, S.G. Shyu, H.S. Sheu, C.H. Chen, C.H. Chuang and M.T. Lin, *Catal. Commun*., **8**, 1060 (2007).
6. W.S. Zhu, H.M. Li, X.Y. He, Q. Zhang, H.M. Shu and Y.S. Yan, *Catal. Commun*., **9**, 551 (2008).
7. S.Y. Ren, Z.F. Xie, L.Q. Cao, X.P. Xie, G.F. Qin and J.D. Wang, *Catal. Commun*., **10**, 464 (2009).
8. P. Blach, Z. Böstrom, S. Franceschi-Messant, A. Lattes, E. Perez and I. Rico-Lattes, *Tetrahedron*, **66**, 7124 (2010).
9. P. Jin, Z.H. Zhao, Z.P. Dai, D.H. Wei, M.S. Tang and X.Y. Wang, *Catal. Today*, **175**, 619 (2011).
10. R. Kamakshi and B.S.R. Reddy, *Catal. Commun*., **8**, 825 (2007).
11. J. Masamoto, K. Hamanaka, K. Yoshida, H. Nagahara, K. Kagawa, T. Iwaisako and H. Komaki, *Angew. Chem. Int. Ed*., **39**, 2102 (2000).
12. D.P. Sawant and S.B. Halligudi, *J. Mol. Catal. A*, **237**, 137 (2005).
13. E. Tsukuda, S. Sato, R. Takahashi and T. Sodesawa, *Catal. Commun*., **8**, 1349 (2007).
14. H. Li, H. Yin, T. Jiang, T. Hu, J. Wu and Y.J. Wada, *Catal. Commun*., **7**, 778 (2006).
15. R. Murugan, M. Karthileyan, P.T. Perumal and B.S.R. Reddy, *Tetrahetron*, **61**, 12275 (2005).
16. J.T. Li, X.H. Zhang and Y.L. Song, *Inter. J. Chem. Technol. Res*., **2**, 341 (2010).
17. (a) T.J. Mason, Practical Sonochemistry, Ellis Horwood Limited: New York (1991); (b) Z.P. Lin, *E-J. Chem*., **9**, 1053 (2012).