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Synthesis of Adipic Acid Catalyzed by Sodium Hypochlorite under Ultrasound Irradiation

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Adipic acid was synthesized from cyclohexanol oxidized by sodium hypochlorite in 94 % yield within 4 h under ultrasound irradiation.

Key Words: Adipic acid, Sodium hypochlorite, Synthesis, Ultrasound irradiation.

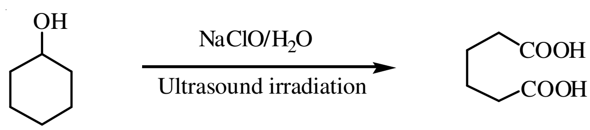
INTRODUCTION

Adipic acid is a most important organic synthetic intermediate and mainly used for synthetic fibers: nylon-66, other fields can also be widely used, for example polyurethane, synthetic resin, leather, polyester foam, plastic plasticizers, lubricants, food additives, adhesives, pesticides, dyes, spices, medicine[1].

The adipic acid was synthesized usually by the oxidation of cyclohexene, cyclohexanol, cyclohexanone or a mixture of them or electro-oxidation of cyclohexanol[2,3], with nitric acid, potassium permanganate, molecular oxygen, ozone as the oxidant. Hydrogen peroxide as a safe, gentle, clean, cheap and readily available oxidant, can replace traditional high-polluting oxidants in organic synthesis. But in these over procedures, the expensive and complex catalysts such as, peroxotungstates and peroxomolybdates[4], ZSM-5 supported metal ions (M/ZSM-5) and *N*-hydroxyphthalimide (NHPI)[5], heteropoly complexes[6], a carbon supported platinum catalyst[7], Ti-AlSBA15 catalysts[8], manganese diimine catalysts[9], Co-substituted β-zeolites catalysts[10], Iron-phthalocyanine on zeolite Y[11], tungstic acid/acidic organic additive[12], phosphotungstic acid[13] *etc*. have to be added in the system.

Sodium hypochlorite also is a common oxidizing and chlorinating agent in various organic syntheses. Its solution is attractive as industrial oxidants, being cheap and containing a high percentage of available oxygen. Moreover, the salt solutions resulting from the reactions, are relatively harmless to the environment and can be electrolyticalty recycled[14].

Ultrasound has increasingly been used in organic synthesis in the last four decades. A large number of organic reactions can be carried out in higher yields, shorter reaction time or milder conditions under ultrasound irradiation. Rothenberg and Sasson[15] reported the oxidative cleavage of cycloalkanones to dicarboxylic acids at 10 ºC using sodium hypochlorite under phase transfer catalysis conditions, but the reaction time was very long to 24 h[15]. In this paper we wish to report an efficient and practical procedure for the synthesis of adipic acid with the oxidation of cyclohexanol by sodium hypochlorite in water under ultrasound irradiation (**Scheme-I**).



Scheme-I

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 kHz, 40 kHz, 59 kHz and a nominal power 250 W).

Typical procedure for the preparation of adipic acid: A 50 mL two-necked round flask was charged with cyclohexanol (2 mmol) and 10 % sodium hypochlorite solution in water (7.4 g, 12 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), during which the pH was maintained at 12.0 by titrating with 0.1 mol/L NaOH. The reaction mixture was extracted with dichloromethane (3 × 15 mL). The aqueous phase was acidified to pH = 2 with 2 M HCl and was left overnight in the ice bath. Adipic acid crystals was obtained, filtered and recrystallized from water to obtain 270 mg, 94 %, m.p.: 152-153 ºC.

RESULTS AND DISCUSSION

In a preliminary experiment, the influence of the amount of sodium hypochlorite solution on the yield was studied. It was found that a molar ratio of cyclohexanol: sodium hypochlorite solution of 1:6 gave the best yield (94 %). By changing the molar ratio to 1:4, 1:5, 1:6.5 and 1:7 the yields decreased to 56, 80, 92 and 88 % respectively (Table-1). The results showed that changing the molar ratio had a significant effect on the yield and the optimum molar ratio of cyclohexanone: sodium hypochlorite solution was 1:6. We found that the more molar amounts of sodium hypochlorite were needed to obtain adipic acid in optimized yield because OCl^- itself decomposes under the reaction conditions.

TABLE-1
EFFECTS OF THE AMOUNT OF SODIUM HYPOCHLORITE ON THE OXIDATION OF CYCLOHEXANOL TO ADIPIC ACID UNDER ULTRASOUND IRRADIATION*

Amount of sodium hypochlorite (g)	4.93	6.17	7.4	8.02	8.63
Yield (%)	56	80	94	92	88

*Ultrasound frequency: 25 kHz; reaction time: 4 h; reaction temperature: 18 ºC

During the reaction, the relative concentrations of HOCl and OCl^- showed a significant effect on the yield. The pH being kept at 12 obtained the optimized yield when $[OCl^-] >> [HOCl]$ (Table-2).

TABLE-2
EFFECT OF pH ON THE OXIDATION OF CYCLOHEXA-NOL TO ADIPIC ACID UNDER ULTRASOUND IRRADIATION*

pH	10	12	12.5	13
Yield (%)	86	94	88	80

*Ultrasound frequency: 25 kHz; amount of sodium hypochlorite solution: 7.4 g; reaction time: 4 h

It was also found that reaction temperature has some effects on the oxidation of cyclohexanol to adipic acid. By changing the reaction temperature from 18 to 15, 20 and 25 ºC the yields decreased from 94 to 93, 89 and 83 % respectively (Table-3). This may be that the lower reaction temperature caused the lower reactivity, but the higher reaction temperature would cause other complex oxidation by-products, moreover, NaOCl solutions decomposed giving Cl_2, O_2 and NaCl. Therefore, the reaction was carried out at 18 ºC under ultrasound irradiation.

TABLE-3
EFFECT OF REACTION TEMPERATURE ON THE OXIDATION OF CYCLOHEXANOL TO ADIPIC ACID UNDER ULTRASOUND IRRADIATION*

Reaction temperature (ºC)	15	18	20	25
Yield (%)	93	94	89	83

*Ultrasound frequency: 25 kHz; amount of sodium hypochlorite solution: 7.4 g; reaction time: 4 h

As shown in Table-4, adipic acid gave a lower yield from the oxidation of cyclohexanol when the reaction time prolonged from 4 to 5 h. The reason may be that the prolonged reaction time would cause many other by-products within the reaction system.

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

Reaction time (h)	3.0	4.0	4.5	5.0
Yield (%)	83	94	92	84

*Ultrasound frequency: 25 kHz; amount of sodium hypochlorite solution: 7.4 g; reaction temperature: 18 ºC

In the absence of ultrasound, on the oxidation of cyclohexanol to adipic acid by sodium hypochlorite solution proceeded in only 76 % yield within 4 h by stirring alone (Table-5). The oxidation gave adipic acid in 94 % yield within 4 h under the ultrasonication of 25 kHz. While under 40 kHz and 59 kHz ultrasound irradiation, the reaction was completed in 4 h with 87 % and 85 % yield respectively. It is apparent that the ultrasound can accelerate the oxidation and lower frequency of ultrasound irradiation improves the yield. Therefore, the reaction was carried out with 25 kHz ultrasound irradiation.

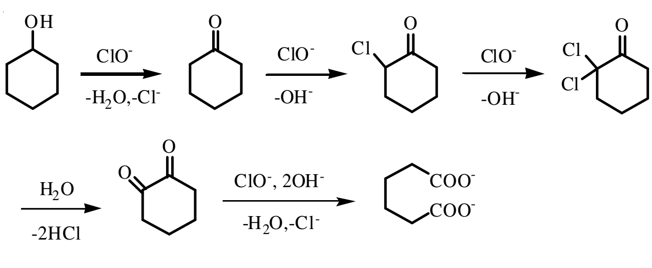
TABLE-5
EFFECT OF ULTRASOUND FREQUENCY ON THE OXIDATION OF CYCLOHEXANOL TO ADIPIC ACID*

Ultrasound frequency (kHz)	25	40	59	Stiring
Yield (%)	94	87	85	76

*Amount of sodium hypochlorite solution: 7.4 g; reaction time: 4 h; reaction temperature: 18 ºC

The adipic acid was synthesized in 63 % from cyclohexanone oxidized by sodium hypochlorite under PTC (trioctylmethylammoniumc hloride) at 10 ºC within 24 h[15]. While in our system, sodium hypochlorite-oxidation reaction was given adipic acid from cyclohexanol in 94 % yields under ultrasound irradiation within 4 h at 18 ºC and without adding the PTC.

The reaction seems to occur *via* a classic oxidative cleavage pathway[15]. The cyclohexanol was oxidized to cyclohexanone at first. Then chlorinating and oxidative reactions completed on the α-position of cyclohexanone and adipic acid was obtained after the cleavage of the bond.



Scheme-II

In summary, we have found an efficient and practical procedure for the synthesis of adipic acid *via* the oxidized by sodium hypochlorite of cyclohexanol under ultrasound irradiation. The present procedure has many advantages such as short reaction time, mild conditions, easy operation procedures and high yields.

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