

Oxidation of cyclic ketones to dicarboxylic acids

Dawid Lisicki, Beata Orlińska*

Silesian University of Technology, Faculty of Chemistry, Department of Chemical Organic Technology and Petrochemistry, Krzywoustego 4, 44-100 Gliwice, Poland

*Corresponding author: e-mail: beata.orlinska@polsl.pl

This paper reports the results of studies concerning an alternative method of obtaining dicarboxylic acids, which consist of the oxidation of cyclic ketones with oxygen or air. The raw materials used were cyclopentanone, cycloheptanone, cyclooctanone, cyclododecanone, 1-tetralon, 2-methylhexanone, 3-methylcyclohexanone and 4-methylcyclohexanone. Oxidation reactions were conducted at 70–100°C, under pressure of 0.1 or 0.4 MPa, for 6 h, utilizing the salts of transition metals as catalyst and acetic acid as solvent. For example, when cyclopentanone was oxidized in the presence of Mn(II) salt, a conversion above 98% and selectivity to glutaric acid up to 68% were obtained. Among synthesized dicarboxylic acids, 1,12-dodecanoic acid was obtained with the highest selectivity of 76%.

Keywords: Dicarboxylic acids, cyclic ketones, oxidation, cyclopentanone, glutaric acid.

INTRODUCTION

Saturated dicarboxylic acids are an important group of organic compounds. On an industrial scale, there are produced acids such as oxalic (600 000 tons/year), malonic (70 000 tons/year), adipic (2.7 mln tons/year), cork, azelaic (10 000 tons/year), sebacic and 1,12-dodecanedioic (25–50 000 tons/year)^{1–3}. These acids are used in the production of polyamides and polyesters in the food, cosmetics and pharmaceutical industries⁴. Due to their structure, dicarboxylic acids are additionally used in the production of polyurethanes, plasticisers and polyester polyols.

In the industry, dicarboxylic acids are obtained as a result of the oxidation of cyclic ketones and/or alcohols with use of the nitric acid, oxidative cleavage of unsaturated

dicarboxylic acids, hydrogenation of unsaturated diacids, or esterification of dicarboxylic acids, followed by electrolysis and hydrolysis¹. The raw materials used in the process of forming dicarboxylic acids are primarily obtained from benzene (Fig. 1), butadiene (Fig. 2) and higher unsaturated carboxylic acids occurring naturally (Fig. 3). Most dicarboxylic acids and their derivatives occur in nature, but their isolation has no commercial significance.

Cyclic ketones and alcohols, the raw materials used in dicarboxylic acids synthesis, are primarily obtained as a result of air oxidation of cycloalkanes^{5–8}. In the industrial process, alternative methods are additionally used to obtain cyclic ketones and alcohols consisting of the hydrogenation of unsaturated alcohols or ketone, thermal

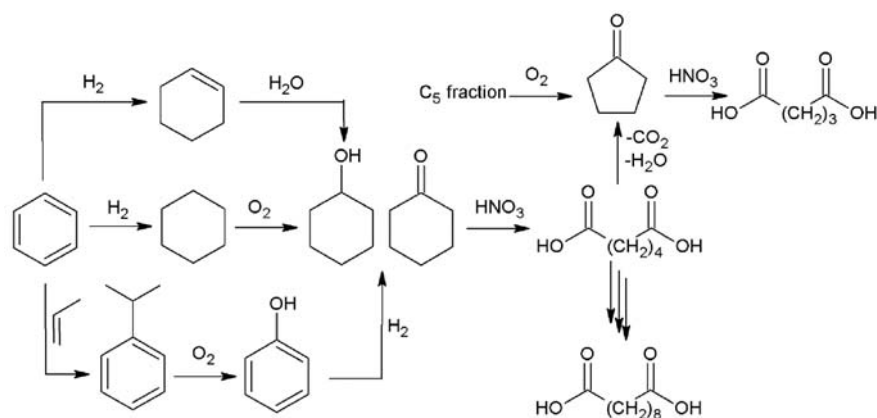


Figure 1. Industrial methods for obtaining dicarboxylic acids from benzene and C5 cracking fraction

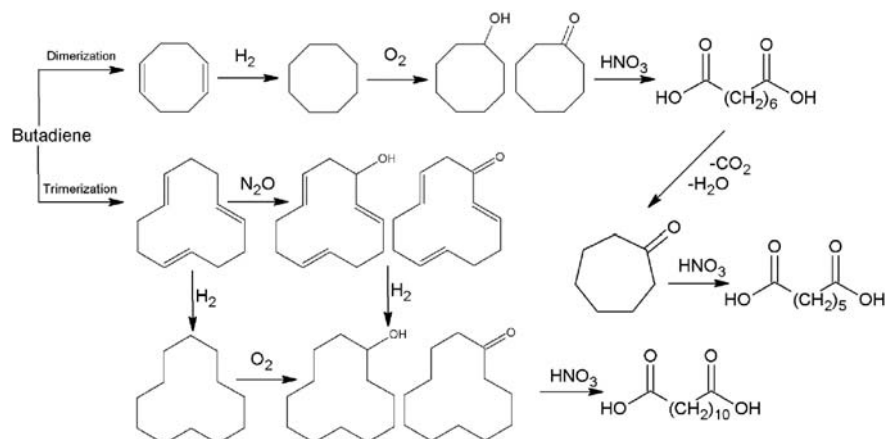


Figure 2. Industrial methods for obtaining dicarboxylic acids from butadiene

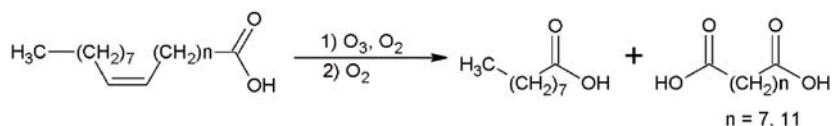


Figure 3. Industrial methods for obtaining azelaic and brassylic acid from oleic and erucic acid

dehydration and the decarboxylation of dicarboxylic acids to lower ketones or hydration of cyclic olefins.

Adipic acid is the most significant dicarboxylic acid in the industry, and its market in 2014 was valued at 6.4 billion dollars⁹. The major method of production of adipic acid is the two-stage process using cyclohexane as a raw material¹⁰. In the first step, cyclohexane is oxidized with air to a mixture of cyclohexanone and cyclohexanol, and cyclohexanone and/or cyclohexanol is reacted with 50–60% nitric acid to adipic acid¹¹.

In most methods of dicarboxylic acid production from petrochemical raw materials, cyclic ketones and alcohols are oxidized with 50–60% nitric acid and/or nitrogen dioxide. Consequently, large quantities of nitrous oxide¹² are formed, and its reprocessing is difficult to achieve. Nitrous oxide is a greenhouse gas, and it is approximately 300 times more effective than carbon dioxide. Producers of dicarboxylic acids are obliged to utilize or use them. A promising application of nitrous oxide appears to be using it as an oxidizing agent in the process of oxidation of benzene to phenol (AlphOX process)^{13–14}. It is also used in the new BASF process for producing cyclododecanone¹⁰.

Replacing nitric acid with oxygen or air in the process of oxidation of cyclic ketones to dicarboxylic acids appears to be the best solution that contributes to reducing the emission of nitrogen oxides. To date, the oxidation process of cyclohexanone with oxygen/air to adipic acid has been reported in several papers^{15–25}. The processes were usually performed using manganese(II) acetate at atmospheric pressure in acetic acid as solvent. For example, by conducting the oxidation of cyclohexanone process with oxygen in acetic acid, in the presence of Co(II)/Mn(II) system and *p*-toluenesulfonic acid, adipic acid was obtained in 78% yield and 97% conversion (70°C, 0.1 MPa O₂, 5 h)¹⁵. However, a limited number of papers describe research on the oxidation with oxygen process of other cyclic ketones such as cyclopentanone, cycloheptanone, cyclooctanone, cyclododecanone^{26–27} and methyl derivatives of cyclohexanone^{28–32}. The reactions were carried out in the presence of eg.: ruthenium or platinum supported on activated carbon^{27, 29}, natural phosphate modified by vanadium²⁸, [Ru(H₂O)₆]₂(Me-C₆H₄-SO₃)₂³⁰ or commercially available Mn(NO₃)₂/Co(NO₃)₂/HNO₃³¹ system as catalysts. For example, by carrying out the oxidation reaction with oxygen, in the presence of Re₂(CO)₁₀/Peg-400/K₂CO₃/KOH system, adipic acid, pimelic acid, cork acid, acelaic acid and 1,12-dodecanedioic acid were obtained from respective ketones with yields ranging from 74 to 89% (rt., 24–96 h)²⁶. Application of ozone and periodate as oxidizing agents have been also described^{33–34}.

EXPERIMENTAL PART

Raw materials, catalysts, solvents

Cyclopentanone (Aldrich ≥99%), cycloheptanone (Aldrich ≥99%), cyclooctanone (Aldrich ≥98%), cyc-

lododecanone (Merck ≥98%), 2-methylcyclohexanone (Aldrich ≥98%), 3-methylcyclohexanone (Aldrich ≥97%), 4-methylcyclohexanone (Aldrich ≥99%), 1-tetralon (Aldrich 97%), manganese(II) acetylacetonate (Aldrich 99%), manganese(III) acetylacetonate (Aldrich 99%), cobalt(II) acetylacetonate (Aldrich 97%), manganese(II) acetate tetrahydrate (Aldrich 99.99%), manganese(III) acetate (Aldrich 97%), cobalt(II) acetate tetrahydrate (Aldrich 99.99%), sulfuric acid (Chempur 95%), methanol (Chempur 99.8%), acetic acid (Chempur 99.5%), succinic acid (Aldrich ≥ 99%), glutaric acid (Aldrich 99%), adipic acid (Aldrich ≥99%), pimelic acid (Aldrich 98%), suberic acid (Aldrich 98%), 1,11-undecanedioic acid (Aldrich 97%), 1,12-dodecanedioic acid (Aldrich 99%), 3-methyladipic acid (Aldrich 99%), 2-methyladipic acid (Aldrich 98%), 2-methylglutaric acid (Aldrich 98%), 3-methylglutaric acid (Aldrich 99%), 6-oxoheptanoic acid (Aldrich 90%) were used without purification.

Oxidation at atmospheric pressure

To a thermostat-controlled reactor with a working volume of 120 ml (height 19.5 cm, diameter 2.8 cm) and equipped with a reflux condenser and a bubbling system, 80 ml of respective cyclic ketone and acetic acid (ketone : acetic acid 1:4 or 1:6 v/v) and catalyst (0.05–0.5 mol %) were introduced. The mixture was heated to the oxidation reaction temperature, and the air or oxygen was introduced through a bubbler with a G3 ceramic sinter (12 l/h). The flow of the oxidizing agent was controlled by the BETA-ERG electronic mass flow controller. The conversion and selectivity of major products were determined based on GC FID analysis.

Oxidation under pressure

To a pressure reactor (Autoclave Engineers Inc. USA) with a volume of 100 ml, made of Hastelloy C-276 steel and equipped with a reflux condenser, high-speed turbine agitator, heating jacket and an internal cooler, 4 ml of cyclopentanone, 16 ml of acetic acid and Mn(acac)₂ (0.1 mol %) were introduced. The mixture was heated to 100°C and oxygen was introduced to 0.4 MPa. The temperature, pressure and speed of the stirrer were monitored using a Sentinel control device. During the reaction, the pressure decrease due to oxygen consumption was supplemented with additional amounts of oxygen. The conversion and selectivity of major products were determined based on GC FID analysis.

Analytical methods

A GC analysis of products was performed using a Hewlett 5890 Series II Gas Chromatograph equipped with an FID detector, an automatic sample dispenser and a Zebron ZB-5HT column (30 m × 0.25 mm × 0.25 μm) and helium as a carrier gas. The composition of post-reaction mixtures was determined using the internal standard method (toluene) (injection port temperature 200°C, detector temperature 300°C, split 100:1, injec-

tion 1 μ l, air 400 ml/min, nitrogen 24 ml/min, hydrogen 30 ml/min, temperature program 70°C for 10 min, 6°C/min to 112°C, 20°C/min to 212°C, 8 min at 212°C). The dicarboxylic acid content was determined in the form of their methyl diesters obtained by esterification of the post-reaction mixture. The esterification reaction was conducted at an ambient temperature for 24 h with methanol, utilizing catalytic amounts of sulfuric acid (for 1 g of the sample, 14 ml of methanol and 5 drops of sulfuric acid were used). Each sample was analysed twice, before and after esterification, for determination of raw material and obtained acids, resp.

The products composition was additionally confirmed by GC MS performed using an Agilent gas chromatograph 7890C (Agilent HP-5 MS capillary column, 30 m \times 0.25 mm \times 0.25 μ m, helium 1 mL/min) coupled with an Agilent mass spectrometer 5975C with EI ionization (70 eV) using the NIST/EPA/NIH Mass Spectral Library.

RESULTS AND DISCUSSION

This study evaluated the oxidation of cyclic ketones with air or oxygen at pressures of 0.1 or 0.4 MPa, utilizing the acetylacetonates or acetates of manganese(II), manganese(III) and cobalt(II) in acetic acid. The raw materials used in the process were cyclopentanone, cycloheptanone, cyclooctanone, cyclododecanone, 1-tetralon, 2-methylhexanone, 3-methylcyclohexanone and 4-methylcyclohexanone. The selection of the substrate was justified by the potential industrial significance of the studied process. Oxidation reactions were conducted at a temperature of 70–100°C for 6 h.

Table 1 presents the results of the research on the oxidation reaction of cyclopentanone under various conditions.

The main product of cyclopentanone aerobic oxidation, as expected, was glutaric acid (GA). The probable mechanism of its formation is presented in Figure 4. GC MS analysis showed that post-reaction mixtures contained also succinic acid and in lower amount hydroxy or oxo derivatives of pentanoic and butanoic acids.

It was demonstrated that all tested metal compounds showed the activity in the oxidation reaction of cyclopentanone to glutaric acid (GA). Higher conversion, as well as selectivity to GA, was achieved in the presence of manganese than cobalt salt. Utilizing the manganese salts, a high conversion of cyclopentanone was obtained, above 98%, and glutaric acid was obtained with selectivity in the range from 42 to 45. The reaction utilizing the cobalt salt enabled the attainment of glutaric acid with a selectivity of 28–30% and the conversion of cyclopentanone in a range from 75 to 80%.

Increasing the volume ratio of cyclopentanone to acetic acid from 1:4 to 1:6 only slightly affects the increase of oxidation to glutaric acid selectivity from 42% to 45%, possibly due to the good solubility of glutaric acid in acetic acid³⁵. The positive effect of using larger amount of solvent possibly could be observed in the synthesis of less soluble acids when the precipitation of products could hinder the contact between gaseous and liquid reagents.

An increase in selectivity of glutaric acid was observed when air was replaced by oxygen, as well as when the pressure was increased from atmospheric to 0.4 MPa.

Table 1. Oxidation of cyclopentanone

Entry	Catalyst		Pressure [MPa]	Temp. [°C]	$V_{CP}:V_{AcOH}^c$	α [%]	S_{GA} [%]	S_{BA} [%]
	Type	[mol %]						
1	–	–	0.1	100	1 : 4	0	0	0
2	Mn(acac) ₂	0.05	0.1	100	1 : 4	83	41	12
3	Mn(acac) ₂	0.1	0.1	100	1 : 4	100	42	7
4	Mn(acac) ₂	0.5	0.1	100	1 : 4	100	43	12
5	Mn(acac) ₃	0.1	0.1	100	1 : 4	98	44	9
6	Co(acac) ₂	0.1	0.1	100	1 : 4	75	30	8
7	Mn(OAc) ₂	0.1	0.1	100	1 : 4	100	45	10
8	Mn(OAc) ₃	0.1	0.1	100	1 : 4	98	42	10
9	Co(OAc) ₂	0.1	0.1	100	1 : 4	80	28	9
10	Mn(acac) ₂ Co(acac) ₂	0.05 0.05	0.1	100	1 : 4	97	38	32
11	Mn(acac) ₂	0.1	0.1	100	1 : 6	100	45	9
12 ^a	Mn(acac) ₂	0.1	0.1	100	1 : 4	97	52	11
13 ^b	Mn(acac) ₂	0.1	0.4	100	1 : 4	100	68	11
14	Mn(acac) ₂	0.1	0.1	70	1 : 4	84	46	10
15	Mn(acac) ₂	0.1	0.1	80	1 : 4	97	54	9

Cyclopentanone (CP) and acetic acid 80 ml, air 0.1 MPa, 12 l/h, 6 h, a – oxygen 0,1 MPa, 12 l/h, b – oxygen 0,4 MPa, c – CP : acetic acid ratio (v/v), α – conversion of CP, S_{GA} – selectivity of glutaric acid, S_{BA} – selectivity of succinic acid

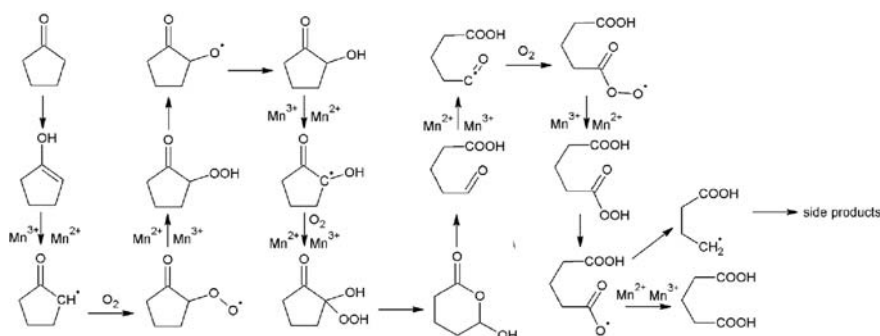


Figure 4. Probable mechanism of oxidation cyclopentanone to glutaric acid, based on¹⁵

However, the application of oxygen in industrial synthesis can be limited because of safety concerns.

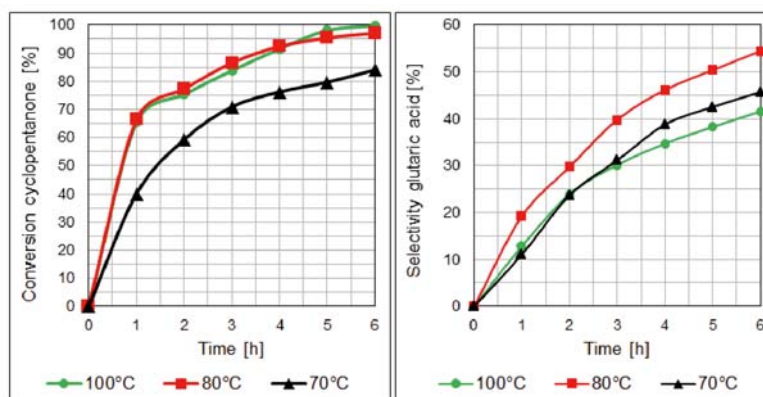
The effect of temperature in the range of 70–100°C on glutaric acid selectivity and conversion was evaluated (Table 1, entries 3,14,15; Fig. 5). The highest GA selectivity of 54% was obtained at 80°C. The oxidation of cyclic ketones to dicarboxylic acids is a multistep process consisting of several subsequent and parallel reactions²⁰. Possibly, at 100°C, the share of side reactions leading to shorter acids increased. On the other hand, the rate of subsequent steps of cyclopentanone oxidation leading from cyclopentanone to GA decreased at 70°C. On the basis of the GC MS analysis, it was found that the product contained higher amounts of semi-products.

Table 2 presents the results of the research on the oxidation reaction of a series of cyclic ketones to the corresponding acids in the presence of Mn(II) acetylacetonate with air as the oxidizing agent. Using cyclopentanone, cycloheptanone, cyclooctanone and cyclododecanone as

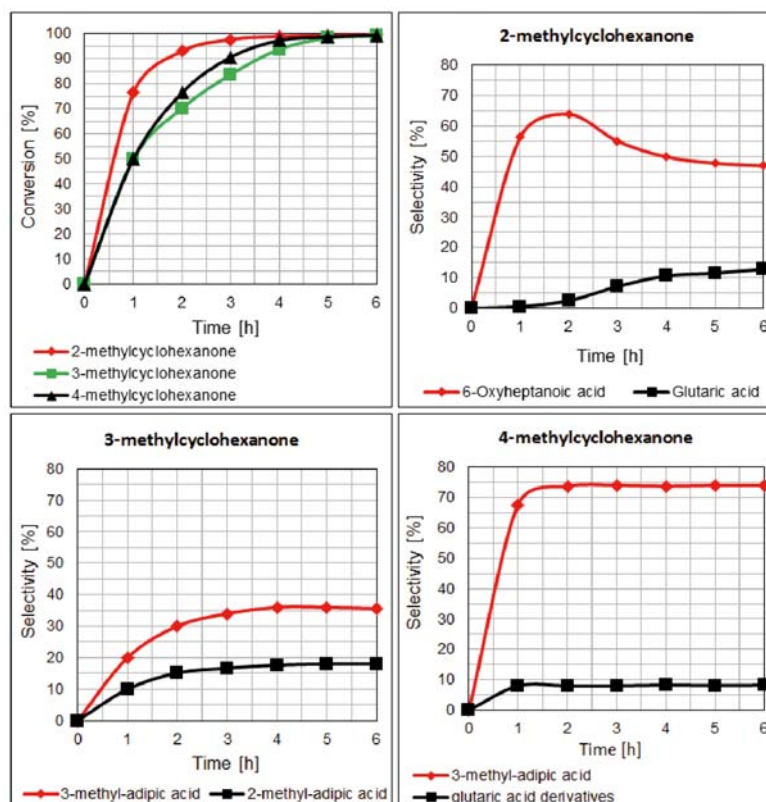
the major products, respectively, glutaric, pimelic, cork and 1,12-dodecanedioic acids were obtained, while shorter dicarboxylic acids were the major by-products. The position of the methyl substituent in cyclohexanone affects the type of products obtained. In the oxidation reaction of 3-methylcyclohexanone and 4-methylcyclohexanone, the products obtained primarily consisted of dicarboxylic acids and their methyl derivatives with 5 and 6 carbon atoms. When 2-methylcyclohexanone was oxidized, 6-oxyheptanoic acid was obtained as the major product. 1-Tetralon did not undergo oxidation reaction under the tested conditions.

Dependence of major product selectivity and conversion of raw materials on the time of oxidation reaction of the methyl derivatives of cyclohexanone are presented in Figure 6.

The position of the methyl substituent in cyclohexanone influenced the rate of oxidation reaction of the raw material. For 2-methylcyclohexanone, the highest oxidation reaction rate was observed. 6-Oxyheptanoic acid was ob-



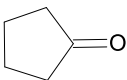
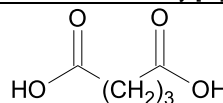
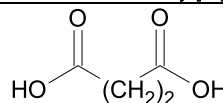
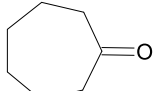
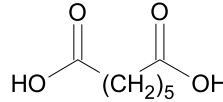
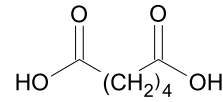
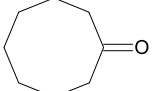
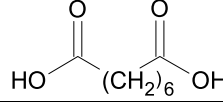
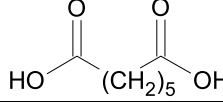
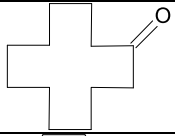
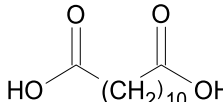
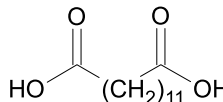
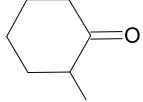
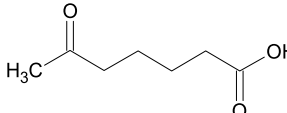
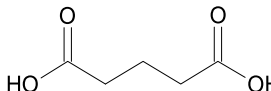
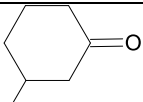
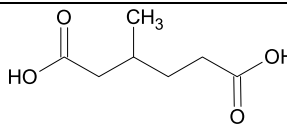
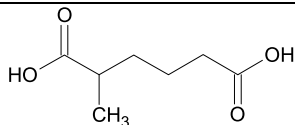
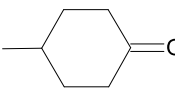
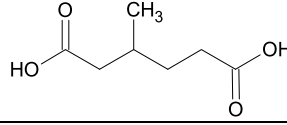
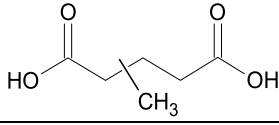
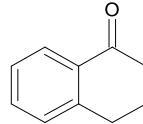
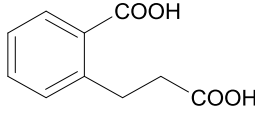
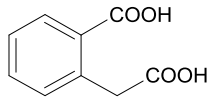
Cyclopentanone 16 ml (15.2 g), acetic acid 64 ml (67.2 g), Mn(acac)₂ 0.1 mol %, air 0.1 MPa, 12 l/h
Figure 5. Influence of temperature on the cyclopentanone oxidation reaction



Ketone 16 ml, acetic acid 64 ml, Mn(acac)₂ 0.1 mol %, air 0.1 MPa, 12 l/h, 6 h, 100°C

Figure 6. The effect of the methyl substituent position on the methylcyclohexanone oxidation reaction

Table 2. Oxidation cyclic ketones to carboxylic acid

Entry	Substrate Conversion [%]		Main product Selectivity [%]		By-product Selectivity [%]	
	Structure	Conversion	Structure	Selectivity	Structure	Selectivity
1 ^a		100		42		7
2 ^b		68		67		15
3 ^c		59		76		13
4 ^d		69		44		13
5 ^e		99		47		13
6 ^f		99		36		17
7 ^g		99		72		16
8		0		0		0

Ketone 16 ml, acetic acid 64 ml, Mn(acac)₂ 0.1 mol %, air 0.1 MPa, 12 l/h, 6 h, 100°C

Other by-products determined based on GC MS analysis:

a – hydroxy and oxo derivatives of pentanoic and butanoic acids

b – glutaric acid, hydroxy and oxo derivatives of pimelic acid, heptanoic acid, hexanoic acid and pentanoic acid

c – adipic acid, glutaric acid, succinic acid, hydroxy and oxo derivatives of cork acid and octanoic acid

d – 1,11-undecanedioic acids, sebacic acid, azelaic acid, cork acid, pimelic acid, adipic acid

e – adipic acid, 2-methyladipic acid, 2-methylglutaric acid, hydroxy and oxo derivatives of hexanoic acid and butanoic acid

f – glutaric acid, hydroxy derivatives of pentanoic acid

g – 2-methylglutaric acid, oxo derivative of pentanoic acid

tained as the major product with the maximum selectivity of 64% achieved after 2 h of the oxidation reaction. It further oxidized in subsequent reactions, most possibly to glutaric acid. As a result of the oxidation reaction of 3-methylcyclohexanone, the major products were 3-methyl-adipic and 2-methyl-adipic acid. The contribution of these products showed that the cleavage of C1-C6 bond occurred more likely than C1-C2 bond. The oxidation of 4-methylcyclohexanone led to primarily obtaining the 4-methyl adipic acid with high 72% selectivity.

CONCLUSIONS

This paper reports the results of studies evaluating an alternative method of obtaining dicarboxylic acids, which consists of the oxidation of cyclic ketones with oxygen or air. It was demonstrated that it is possible to obtain the respective dicarboxylic acids with relatively high selectivity when the oxidation reactions employ these oxidants under relatively mild conditions (100°C, 6 h, 0.1 MPa) in the presence of manganese(II) salt as the catalyst and acetic

acid as the solvent. The respective dicarboxylic acids were obtained when cyclopentanone, cycloheptanone, cyclooctanone, cyclododecanone, 3-methylcyclohexanone and 4-methylcyclohexanone were oxidized under these conditions. The oxidation of 2-methylhexanone led to 6-oxohexanoic acid as the major product.

The proposed method of synthesizing dicarboxylic acids using air is simpler than previously reported methods using oxygen or air as an oxidizing agent (commercially available and cheap catalyst, short reaction time). This method may develop into a future alternative to the traditional methods, which use nitric acid.

LITERATURE CITED

- Cornils, B. & Lappe, P. (2010). *Dicarboxylic Acids, Aliphatic. Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim.
- (2018, February). *Malic Acid Market Size, Share, Trend Analysis Report By End-use (Beverage, Confectionery, Personal Care & Cosmetics), By Region, Competitive Landscape, And*

Segment Forecasts, 2014–2024. Retrieved March 03, 2018, from <https://www.grandviewresearch.com/industry-analysis/malic-acid-market>

3. (2015, November). Another biobased dicarboxylic acid moves toward commercial production, by Verdezyne. Retrieved March 03, 2018, from <https://www.biobasedpress.eu/2015/11/another-biobased-dicarboxylic-acid-comes-into-commercial-production-by-verdezyne>

4. (2017, June). Adipic Acid. Chemical Economics Handbook. Retrieved March 03, 2018, from <https://ihsmarkit.com/products/adipic-acid-chemical-economics-handbook.html>

5. Krzysztoforski, A., Wojcik, Z., Pohorecki, R. & Baldyga, J. (1986). Industrial contribution to the reaction engineering of cyclohexane oxidation. *Ind. Eng. Chem. Process Des. Dev. Industrial* 25(4), 894–898. DOI: 10.1021/i200035a010.

6. Oczkiewicz, S., Rygiel S., Wais, J., Koziol, A., Gruszka, M., Kondrat, A., Pohorecki, R., Wierzchowski, P., Moniuk, W., Krzysztoforski, A., Mijal, W., Wójcik, Z. & Zylinski, M. (2006). EP Patents No. 1,720,641. Paris, European Patent Office.

7. Weissermel, K. & Arpe, H.J. (1997). *Industrial Organic Chemistry (3 th ed.)*. New York, British Library Cataloguing

8. Krzysztoforski, A. & Rygiel, S. (2016). Produkcja cykloheksanonu. Od fenolu do benzenu i z powrotem? *Przem. Chem.* 6(95), 1049–1248. DOI: 10.15199/62.2016.6.1

9. (2015, September). Global Markets for Adipic Acid. Retrieved March 03, 2018, from <http://www.researchandmarkets.com/reports/3641969/global-markets-for-adipic-acid#relc2>

10. Teles, J.H., Hermans, I., Franz, G. & Sheldon R.A. (2015). Oxidation. *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim.

11. Lisicki, D., Dobras, G., Orlińska, B. & Zawadiak, J. (2017). Metody otrzymania kwasu adypinowego o potencjalnym zastosowaniu przemysłowym. *Przem. Chem.* 96(7), 1485–1489. DOI: 10.15199/62.2017.7.7.

12. Cavani, F. & Teles, J.H. (2009). Sustainability in catalytic oxidation: An alternative approach or a structural evolution? *Chem. Sus. Chem.* 2(6), 508–534. DOI: 10.1002/cssc.200900020.

13. (1998, December). One Step Phenol from Benzene by the AlphOx Process. Retrieved March 03, 2018, from <https://ihsmarkit.com/products/chemical-technology-pep-reviews-one-step-phenol-from-benzene-1998.html>

14. Notté, P.P. (2000). The AlphOx™ process or the one-step hydroxylation of benzene into phenol by nitrous oxide. Understanding and tuning the ZSM-5 catalyst activities. *Top. Catal.* 13, 387–394. DOI: 10.1023/A:1009015223793.

15. Shimizu, A., Tanaka, K., Ogawa, H., Matsuoka, Y., Fujimori, M., Nagamori, Y., Hamachi, H. & Kimura, K. (2003). An Industrial Process for Adipic Acid Production by the Liquid-Phase Oxidation of Cyclohexanone with Molecular Oxygen. *Bull. Chem. Soc. Jpn.* 76(10), 1993–2001. DOI:10.1246/bcsj.76.1993.

16. Kamath, S.S. & Chandalia, S.B. (1973). Liquid phase oxidation of cyclohexanone to adipic acid by air in acetic acid solution. *J. Appl. Chem. Biotechnol.* 23(6), 469–478. DOI: 10.1002/jctb.5020230610.

17. Rao, D.G. & Raghunathan, T.S. (1984). Oxidation of Cyclohexanone to Adipic Acid with a Cobalt Acetate/Oxygen/Acetic Acid System. *J. Chem. Tech. Biotechnol.* 34A, 381–386. DOI: 10.1002/jctb.5040340705.

18. Atlamsani, A., Brégeault, J.M. & Ziyad, M. (1993). Oxidation of 2-Methylcyclohexanone and Cyclohexanone by Dioxygen Catalyzed by Vanadium-Containing Heteropolyanions. *J. Org. Chem.* 58(21), 5663–5665. DOI: 10.1021/jo00073a026.

19. Iwahama, T., Syojyo, K., Sakaguchi, S. & Ishii, Y. (1998). Direct Conversion of Cyclohexane into Adipic Acid with Molecular Oxygen Catalyzed by N-Hydroxyphthalimide Combined with Mn(acac)₂ and Co(OAc)₂. *Org. Process Res. Dev.* 2(4), 255–260. DOI: 10.1021/op980016y.

20. Zou, G., Zhong, W., Mao, L., Xu, Q., Xiao, J., Yin, D., Xiao, Z., Kirk, S.R. & Shu, T. (2015). A non-nitric acid method of adipic acid synthesis: Organic solvent- and promoter-free

oxidation of cyclohexanone with oxygen over hollow-structured Mn/TS-1 catalysts. *Green Chem.* 17(3), 1884–1892. DOI: 10.1039/c4gc02333a.

21. Flemming, W. & Speer W. (1935). U.S. Patent No. 2,005,183.

22. Flemming W. (1942). U.S. Patent No. 2,299,013.

23. Ralph, H.C. & Bergenfield, N.J. (1965). U.S. Patent Np. 3,207,783.

24. Baker R.S., Washington, P. & Cohen M.A. (1966). U.S. Patent Np. 3,234,271.

25. Lidov, R.E. & Neck G.N.Y. (1968). U.S. Patent Np. 3,361,806.

26. Osowska-Pacewicka, K. & Alper, H. (1988). Oxidation of Cyclic Ketones Catalyzed by Polyethylene Glycol and Rhenium Carbonyl under Basic and Exceptionally Mild Conditions, *J. Org. Chem.* 2(1), 808–810. DOI: 10.1021/jo00239a023.

27. Besson, M., Gallezot, P., Perrard, A. & Pinel, C. (2005). Active carbons as catalysts for liquid phase reactions. *Catal. Today*, 102–103, 160–165. DOI: 10.1016/j.cattod.2005.02.037.

28. Dakkach, M., Atlamsani, A. & Sebti, S. (2012). Le phosphate naturel modifié au vanadium : un nouveau catalyseur pour l'oxydation des cycloalcanones et des α -cétols en présence de l'oxygène moléculaire. *C. R. Chimie* 15(6), 482–492. DOI: 10.1016/j.crci.2012.03.003.

29. Besson, M., Gauthard, F., Horvath, B. & Gallezot, P. (2005). Catalytic oxidation with air of cyclohexanone to dicarboxylic acids on synthetic carbons. Effect of supported metals and solvents. *J. Phys. Chem. B* 109(6), 2461–2467. DOI: 10.1021/jp0459662.

30. Vennat, M. & Brégeault, J.M. (2010). Oxidative cleavage of cycloalkanones with dioxygen catalyzed by supported catalysts or homogeneous systems: Evidence for novel active ruthenium (II) and/or (III) species. *Appl. Catal. A-Gen.* 386(1–2), 9–15. DOI: 10.1016/j.apcata.2010.07.016.

31. Fumagalli, C., Minisci, F. & Pirola, R. (2001). W.O. Patent No. 01,87815. World Intellectual Property Organization.

32. Vennat, M., Bregeault, J.M. & Herson, P. (2004). Mixed crystals containing the dioxo complex $[[\text{Ph}_3\text{SiO}]_2\text{VO}_2]$ - and novel pentacoordinated oxoperoxo complex $[[\text{Ph}_3\text{SiO}]_2\text{VO}(\text{O}_2)]$ -: X-ray crystal structure and assessment as oxidation catalysts. *Dalton Trans.* (6), 908–13. DOI: 10.1039/b400657g.

33. Syroezhko, A.M. & Begak, O.Yu. (2004). Ozonolysis of Methylcyclohexanols and Methylcyclohexanones. *Russian J. Appl. Chem.* 77(1), 102–105. DOI: 10.1023/B:R-JAC.0000024586.74168.99.

34. Renukdas, S.V., Patil, S. & Patel, N.T. (2014). Kinetics of oxidation of 3-methyl cyclohexanone by periodate catalyzed by Ru(III) in alkaline medium. *Physical Chem.* 9(4), 141–143.

35. Song, W., Ma, P., Fan, L. & Xiang, Z. (2007). Solubility of Glutaric Acid in Cyclohexanone, Cyclohexanol, Their Five Mixtures and Acetic Acid. *Chin. J. Chem. Eng.* 15(2), 228–232. DOI: 10.1016/S1004-9541(07)60063-9.