

Article

Selective Oxidation of Cyclohexanone to Adipic Acid Using Molecular Oxygen in the Presence of Alkyl Nitrites and Transition Metals as Catalysts

Dawid Lisicki ^{1,*}, Beata Orlińska ^{1,*}, Tomasz Martyniuk ², Krzysztof Dziuba ² and Jakub Bińczak ²

¹ Department of Chemical Organic Technology and Petrochemistry, Silesian University of Technology, Akademicka 2A, 44-100 Gliwice, Poland

² Grupa Azoty Zakłady Azotowe "Puławy" S.A., Al. Tysiąclecia Państwa Polskiego 13, 24-110 Puławy, Poland; tomasz.martyniuk@grupaazoty.com (T.M.); krzysztof.dziuba@grupaazoty.com (K.D.); jakub.binczak@grupaazoty.com (J.B.)

* Correspondence: dawid.lisicki@polsl.pl (D.L.); beata.orlinska@polsl.pl (B.O.)

Abstract: This paper presents a not previously reported catalytic system consisting of transition metals Co^{2+} and Mn^{2+} and alkyl nitrites R-ONO for the oxidation of cyclohexanone with oxygen to adipic acid. The influence of type and amount of catalyst, temperature, time, and type of raw material on conversion and product composition were determined. In addition, the oxidation of selected cyclic ketones such as cyclopentanone, cyclohexanone, cyclooctanone, cyclododecanone, 2-methylcyclohexanone, 3-methylcyclohexanone, and 4-methylcyclohexanone in acetic acid as solvent was performed. The results showed that R-ONO systems, under established reaction conditions, form NO-radicals, which oxidize to NO_2 under a strong oxidation reaction environment. The $\text{Co}^{2+}/\text{Mn}^{2+}/\text{NO}_2$ system was shown to be highly active in the oxidation of cyclic ketones with oxygen.

Keywords: green chemistry; industrial synthesis; adipic acid; oxidation



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1. Introduction

Aliphatic dicarboxylic acids are used, inter alia, in the production of polyamides, plasticizers, and polyesters. Dicarboxylic acids such as adipic acid (AA), glutaric acid (GA), cork, and 1,12-dodecanedioic acid are mainly produced via the oxidation of cyclic ketones and/or alcohols with HNO_3 [1]. 1,10-decanedioic acid is obtained by esterification of AA, followed by electrolysis and hydrolysis [2]. The methods of dicarboxylic acids production through oxidative cleavage of unsaturated carboxylic acids or hydrogenation of unsaturated diacids are also practiced on industrial scale [3].

Undoubtedly, in industry, AA is considered the most important dicarboxylic acid. In 2014, the AA market was valued at USD 6.5 billion [4], and world production was 2.7 million tons. It has been industrially manufactured since the 1940s via Du Pont technology from cyclohexane [5]. In the first stage of this method, cyclohexane is oxidized to a mixture of cyclohexanol (C-OL) and cyclohexanone (C-ON) with air and in the presence of 0.01–1 ppm $\text{Co}^{2+}/\text{Fe}^{2+}$ (conversion 4–8%, selectivity 70–80%, 0.5–2.0 MPa, 140–180 °C) [6]. In the next stage, the obtained mixture is converted to AA via oxidation with HNO_3 (Figure 1) [7,8].

One of the by-products of this process is N_2O , which is difficult to manage and utilize because it is a powerful greenhouse gas, approx. 300 times stronger than CO_2 , with a half-life of approx. 120 years [9]. As a result of AA production, about 290–310 kg of $\text{N}_2\text{O}/\text{t}_{\text{AA}}$ is obtained [10].

Currently, it is desirable to develop an ecological and economically viable method for the production of dicarboxylic acids [11] that meets specific requirements of sustainable development and principles of green chemistry (high conversion, selectivity, heterogeneous catalysis, use of renewable raw materials [12–16], and elimination of solvents). However, designing technologies that adhere to such restrictions is extremely difficult. As shown

previously [17], AA production from biomass is associated with higher greenhouse gas emissions and higher energy consumption compared to traditional processes using benzene as a petrochemical raw material. Therefore, the replacement of the non-ecological oxidizing agent HNO_3 is the most important issue in dicarboxylic acid production.

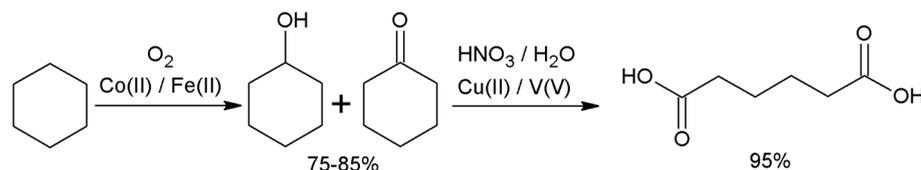


Figure 1. Industry method of AA production from cyclohexane.

The literature has described oxidation processes of cyclohexane directly to AA, with oxygen/air, O_3 [18], and HNO_3 [19], with the main focus being the use of oxygen/air as the oxidizing agent. The reaction is mainly carried out in acetic acid (AcOH) as a solvent and in the presence of transition metal salts or complexes [20]. In order to initiate the process, small amounts of cyclohexanone (C-ON) are introduced [21,22]. Additionally, reports have utilized oxidative organocatalysts such as *N*-hydroxyphthalimide (NHPI) [23–29] and but-2-one (MEK) [30]. Importantly, the oxidation of cyclohexane to AA in the absence of solvent has been studied in the presence of heterogeneous catalysts such as Fe(III)AlPO-31 [31], NHPI/Fe(BTC) [32], Fe(III)T(O-Cl)PP [33] and salts as well as complexes of transition metals in combination with a lipophilic 4-dodecyloxycarbonyl-*N*-hydroxyphthalimide (C_{12} -NHPI) derivative [34]. Oxidation of cyclohexane has been also achieved using a AcOH/ H_2O mixture in the presence of Co/Mn [35] and Mn(III)T(p-Cl)PP [36] clusters in PhCOOH/ H_2O [36] and AcOH/ scCO_2 [37].

It is of particular interest to replace HNO_3 in the oxidation of C-ON and/or C-OL to AA with environmentally friendly oxidizing agents such as oxygen (O_2), air, or H_2O_2 , which eliminates problems related to the management or utilization of the generated NO_x [38]. The use of environmentally friendly oxidizing agents requires the development of catalytic systems capable of obtaining AA with high selectivity. The first patents related to C-ON oxidation under air to AA in the presence of transition metal salts appeared in the 1930s and 1940s [39–43]. Table 1 shows examples of catalysts used in the oxidation of C-ON to AA with O_2 or air.

Table 1. Review of used catalysis and conditions in the oxidation of cyclohexanone to AA with O_2 or air.

Entry	Catalysis System	Solvent	Temp. (°C)	Pressure (MPa)	Time (h)	Conv. (%) ^a	Sel. (%) ^b	Ref.
1	Mn-HTS	-	90	0.6	9	68	93	[44]
2	Pt/carbon	H_2O	140	5.0	-	100	39	[45]
3	Pt/carbon/monolith	H_2O	140	5.0	1	100	21	[46]
4	Modified carbon material	H_2O	140	5.0	6	100	33	[47]
5	Hybrid iron phosphonate material (FePO-1–2)	H_2O	75	0.1	10	96	72	[48]
6	Mn-HTS	AcOH	90	0.6	9	91	86	[44]
7	NHPI/Mn(acac) ₂	AcOH	100	0.1	6	99	64	[26]
8	Co(OAc) ₂ /NaBr	AcOH	80	0.1	1	-	36	[49]
9	Co(OAc) ₂	AcOH	105	0.5	-	98	71	[50]
10	POM Keggin	AcOH/ H_2O	70	1.0	6	18	65	[51]
11	Cluster Co/Mn/MEK ^[c]	AcOH/ H_2O	100	3.8	8	98	87	[35]
12	$\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]\cdot 30\text{H}_2\text{O}$	AcOH/ H_2O	70	0.1	7	99	40	[52]
13	$\text{H}_7[\text{PMo}_8\text{V}_4\text{O}_{40}]\cdot 12\text{H}_2\text{O}$	AcOH/ H_2O	70	0.1	7	99	51	[52]
14	Mn(OAc) ₂ /Co(OAc) ₂ /p-TS ^[d]	AcOH/ H_2O	70	0.1	5	97	78	[53]
15	Mn(NO ₃) ₂ /Co(NO ₃) ₂	AcOH/ H_2O	40	0.1	-	98	93	[54]
16	Nanosheets of Ni-SAPO-34 molecular Sieve	acetone	135	1.5	20	30	87	[55]

^a, conversion C-ON; ^b, AA selectivity; ^c, methyl ethyl ketone; ^d, para-toluenesulfonic acid.

The process of oxidation of C-ON to AA in the presence of O₂ or air was examined previously [53]. The oxidation reaction was carried using transition metals, mainly Co²⁺ and Mn³⁺ acetates or acetylacetonates and para-toluenesulfonic acid (p-TS). The researchers found that the presence of p-TS improved the selectivity of the reaction. For example, when C-ON oxidation was conducted in AcOH (1:7.3 *v:v*) in the presence of H₂O and using the Co²⁺/Mn²⁺ system with p-TS, AA was obtained with 78% selectivity and 99.3% C-ON conversion. The reaction conditions were 5 h reaction time, 1.21 MPa pressure, at 70 °C using a mixture of O₂ (4.9 l/h) and N₂ (48.1 l/h). Additionally, high AA yields have been obtained via oxidation of C-ON with O₂ in the presence of Mn(NO₃)₂/Co(NO₃)₂ [54].

Recently, the beneficial effect of nitrites on the oxidation of hydrocarbons with O₂ has been reported [56]. The authors showed that isoamyl nitrite (IPN) increased the conversion of cycloalkanes (C₅–C₈) via oxidation with O₂ in the presence of the system Co(acac)₂ and or Mn(acac)₂. Others have shown the oxidation of olefins with O₂ using tert-butyl nitrite (TBN) [57–59]. Additionally, reports have shown the oxidation of alcohols to aldehydes and/or ketones with O₂ using TBN in systems with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) [60], TEMPO/HBr ((2,2,6,6-tetramethyl piperidin-1-yl)oxyl) [61], TEMPO/DMC (dichloromethane) [62], 4-OH-TEMPO/TCQ/HCl ((4-hydroxyl (2,2,6,6-tetramethyl piperidin-1-yl)oxyl)/tetrachlorobenzoquinone) [63], MNST/H₂O (2,2,6,6-tetramethylpiperidin-1-yl)oxyl on Fe₃O₄ silicate nanoparticles) [64], IL@SBA-15-TEMPO/AcOH (SBA-15 functionalized, with TEMPO and ionic liquid) [65], DDQ/AcOH/DMC [66], ABNO/KPF₆/H₂O (8-azabicyclo [3.3.1] nonagn-*N*-oxyl) [67], NHPI/MeCN [68], and AZADO/MeCN (2-azaadamantane-*N*-oxyl) [69].

In this study, the influence of alkyl nitrites on the oxidation of cyclic ketones to dicarboxylic acids was demonstrated for the first time. The beneficial effect of the addition of nitrites such as pentyl- (IP), tert-butyl- (TBN), and isopentyl (IPN) nitrite in a system with Co²⁺ and Mn²⁺ on AA selectivity and C-ON conversion was described. The obtained results show that R-ONO systems form NO· radicals, which oxidize to NO₂ in a strongly oxidizing environment. The proposed Co²⁺/Mn²⁺/NO₂ system provided high activity in the oxidation of cyclic ketones with O₂.

2. Materials and Methods

2.1. Materials

The following were used: cyclopentanone (Sigma-Aldrich, St. Louis, MI, USA, ≥99%), cyclohexanone (Sigma-Aldrich, ≥99%), cycloheptanone (Sigma-Aldrich, ≥99%), cyclooctanone (Sigma-Aldrich, ≥98%), cyclododecanone (Merck, Rahway, NJ USA, ≥98%), 2-methylcyclohexanone (Aldrich, St. Louis, MI, USA, ≥98%), 3-methylcyclohexanone (Aldrich, ≥97%), 4-methylcyclohexanone (Aldrich, ≥99%), cyclohexanol (Sigma-Aldrich, >99%), cyclohexane (Sigma-Aldrich, >99%), manganese(II) acetylacetonate (Sigma-Aldrich, 99%), cobalt(II) acetylacetonate (Sigma-Aldrich, 97%), manganese(II) acetate tetrahydrate (Sigma-Aldrich, 99.99%), cobalt(II) acetate tetrahydrate (Sigma-Aldrich, 99.99%), manganese(II) nitrate tetrahydrate (Sigma-Aldrich, ≥97%), cobalt(II) nitrate hexahydrate (Sigma-Aldrich, >99%), isopentyl nitrite (Sigma-Aldrich, 96%), tert-butyl nitrite (Sigma-Aldrich, 90%), N-hydroxyphthalimide (Acros, Waltham, MA, USA, 98%), methyl ethyl ketone (Sigma-Aldrich, 99.7%), nitric acid (Sigma-Aldrich, 60%), pentyl nitrite (Sigma-Aldrich, 98%), acetic acid (Chempur, Karlsruhe, Germany, 99.5%), acetonitrile (Chempur, 99.5%), benzonitrile (Sigma-Aldrich, 99%), sulfuric acid (Chempur, 98%), and methanol (Chempur, 99.8%).

2.2. General Procedure for Catalytic Oxidation under Pressure in 100 mL Volume

The 100 mL oxidation process was carried out in an Autoclave Engineers Inc. pressure reactor, (Erie, PA, USA), made of Hastelloy C-276 steel and equipped with a high-speed stirrer, heating jacket, internal cooler, and reflux condenser. In a typical process, 2 mL of substrate, 20 mL of solvent, and the catalytic system were introduced into the reactor. The reactor contents were purged with O₂ at 2 l/h for 2 min, then heated to 40–100 °C and stirred at 1000 rpm. Subsequently, O₂ was introduced into the reactor under pressure

0.1–1.5 MPa, and the oxidation process was started. The pressure, the stirring speed and temperature were monitored using a Sentinel control device. During the process, the pressure decreased due to O₂ consumption and was supplemented with additional O₂.

2.3. General Procedure for Catalytic Oxidation under Pressure in 600 mL Volume

The oxidation process on 600 mL scale was carried out in a PARR pressure reactor (Moline, IL, USA) made of Hastelloy C-276 steel, equipped with a high-speed stirrer, heating oil jacket, internal cooler, and reflux condenser. Air was introduced into the reactor through a bubble placed under the agitator. In a typical process, 30 mL of C-ON, 300 mL of AcOH, and a catalytic system were introduced into the reactor. The reactor contents were purged with air or O₂ at 50 l/h for 2 min, then heated to 60 °C and stirred at 600 rpm. Subsequently, the oxidizing agent was introduced into the reactor at a pressure of 0.5 MPa, the stirring speed was increased to 1200 rpm, the oxidizing agent blow-through was set to 50 l/h, and the oxidation process was started. The pressure, stirring speed and temperature were monitored using a PARR control device. During the oxidation process, the amount of oxidizing agent and gases introduced and oxygen concentration in the gases were monitored. This information was used to calculate the amount of consumed oxygen.

2.4. General Procedure for Catalytic Oxidation under Atmospheric Pressure

The oxidation process on 120 mL scale was carried out in a thermostatic bubble reactor made of glass and equipped with a G5 glass bubble and reflux condenser. Air was introduced into the reactor through a bubble placed at the bottom of the reactor.

In a typical process, 8 mL of C-ON, 80 mL of AcOH, and a catalytic system were introduced into the reactor. The reactor contents were heated to 60 °C. Subsequently, the oxidizing agent (air) was added into the reactor at a flow of 12 l/h. During the oxidation process, the amount of oxidizing agent added introduced to the reactor and the amount of oxygen in the off-gas were monitored.

2.5. Analytical Methods

The reaction products were analyzed using an Agilent 5890 Series II gas chromatograph equipped with an FID detector, Zebron ZB-5HT column (30 m × 0.25 mm × 0.25 µm) and automatic sample dispenser. Helium was used as the carrier gas. The analysis was performed using the standard method with an internal standard (toluene) (injection port temperature 200 °C, detector temperature 300 °C, split 100:1, injection 1 µL, 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). Each sample was analyzed twice, and the substance concentration was calculated on the basis of previously prepared standard curves. The products composition was additionally confirmed by gas chromatography coupled to mass spectrometry (GC-MS) performed using an Agilent gas chromatograph 7890C (Agilent HP-5 MS capillary column, 30 m × 0.25 mm × 0.25 µm, helium 1 mL/min) coupled with an Agilent mass spectrometer 5975C with EI ionization (70 eV) using the NIST/EPA/NIH Mass Spectral Library.

Raw material conversion: First, 1 mL of sample was taken from the reaction products, and 5 mL of toluene in AcOH solution (6 g of toluene in 250 mL of acetic acid) was added. The prepared solution was analyzed by GC.

Content of dicarboxylic acids: Next, 1 mL of sample was taken from the reaction products, and 12 mL of a toluene/methanol solution (12 g of toluene in 1000 mL of methanol) and 1–3 drops of sulfuric acid (VI) were added. The solution was stirred (200 rpm) for 24 h at ambient temperature to form the methanol esters from carboxylic acids. The prepared solution was analyzed by GC, which determined the amount of dimethyl esters of dicarboxylic acids.

It was found that the error resulting from reproducibility and repeatability amounted to 2%.

3. Results

3.1. Oxidation of C-ON with O₂ to AA Using the Co²⁺/Mn²⁺/R-ONO System

Research was carried out on the oxidation reactions of C-ON to AA using alkyl nitrites R-ONO in the Co²⁺/Mn²⁺ system and, in polar solvents (AcOH), acetonitrile (MeCN) or benzonitrile (PhCN). IPN, amyl nitrite (PN), and TBN were used in the research. A reaction was performed using HNO₃ for comparison. In the reaction products, the content of C-ON (AA) and the main by-product (GA) was determined. The reaction was carried out at 50–120 °C, for 2–6 h, under pressure of 0.5–1.5 MPa O₂ (Figure 2). The results of the various experiments are presented in Table 2.

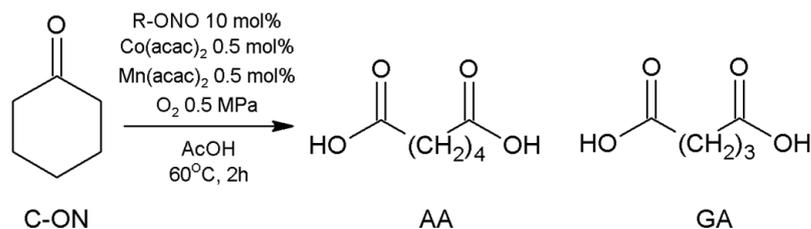


Figure 2. Aerobic oxidation of C-ON.

The results show that under the tested conditions (60 °C, 0.5 MPa O₂), the addition of each R-ONO increased C-ON conversion. Addition of IPN and TBN increased AA selectivity (entries 5, 7), where the IPN/Co²⁺/Mn²⁺ system gave 62% selectivity and 97% C-ON conversion (entry 5). In the case of the Co²⁺/Mn²⁺ system, AA was obtained with 42% selectivity and 68% C-ON conversion (entry 1).

Interestingly, the C-ON oxidation process occurred even under mild reaction conditions (60 °C) and catalyzed solely with IPN (entry 2). This highlights IPN high activity as an organocatalyst. To our knowledge, this is the first example of oxidation of cyclic ketones without the participation of metal catalysts. Examination of Co²⁺ and Mn²⁺ compounds revealed no significant differences in reaction outcome (entries 9, 10). Furthermore, addition of HNO₃ increased C-ON conversion and AA selectivity (entry 8). However, the IPN/Co²⁺/Mn²⁺ system provided AA in higher selectivity. The observed variation in selectivity may stem from NO₂ generation from R-ONO and HNO₃, where R-ONO at 60 °C decomposes to R-O· and NO·. However, under strongly oxidizing conditions, NO· undergoes spontaneous oxidation to NO₂, which contributes to the oxidation reaction. In the case of HNO₃, an equilibrium forms between NO₂, O₂, and H₂O, and under high pressure (0.5 MPa), this equilibrium shifts towards HNO₃, which results in lower activity of the HNO₃/Co²⁺/Mn²⁺ system.

Table 2. Aerobic oxidation of cyclohexanone in the presence of R-ONO/Co²⁺/Mn²⁺.

Entry	Initiator	Mn ²⁺	Co ²⁺	Conv. (%) ^a	Sel. AA (%)	Sel. GA (%)
1	-	0.5	0.5	68	42	16
2	IPN	-	-	38	45	10
3	IPN	0.5	-	94	56	13
4	IPN	-	0.5	66	43	12
5	IPN	0.5	0.5	97	62	19
6	PN	0.5	0.5	96	43	14
7	TBN	0.5	0.5	89	51	16
8	HNO ₃	0.5	0.5	96	54	18
9 ^b	IPN	0.5	0.5	95	59	19
10 ^c	IPN	0.5	0.5	92	58	18

C-ON 2 mL (19.3 mmol), AcOH 20 mL (349.7 mmol), initiator 10 mol%, Co(acac)₂ 0.5 mol%, Mn(acac)₂ 0.5 mol%, 60 °C, O₂ 0.5 MPa, 2 h; ^a, conversion of C-ON; ^b, Co(NO₃)₂ and Mn(NO₃)₂; ^c, Co(OAc)₂ and Mn(OAc)₂.

In the case of the IPN/Co(acac)₂/Mn(acac)₂ catalytic system, which generates AA in the highest selectivity, the influence of basic parameters on the composition of C-ON oxidation reaction products was determined. Figure 3 shows the influence of IPN amount (1–20 mol%) on C-ON conversion and AA and GA selectivity. For comparison, the reaction without IPN addition was conducted.

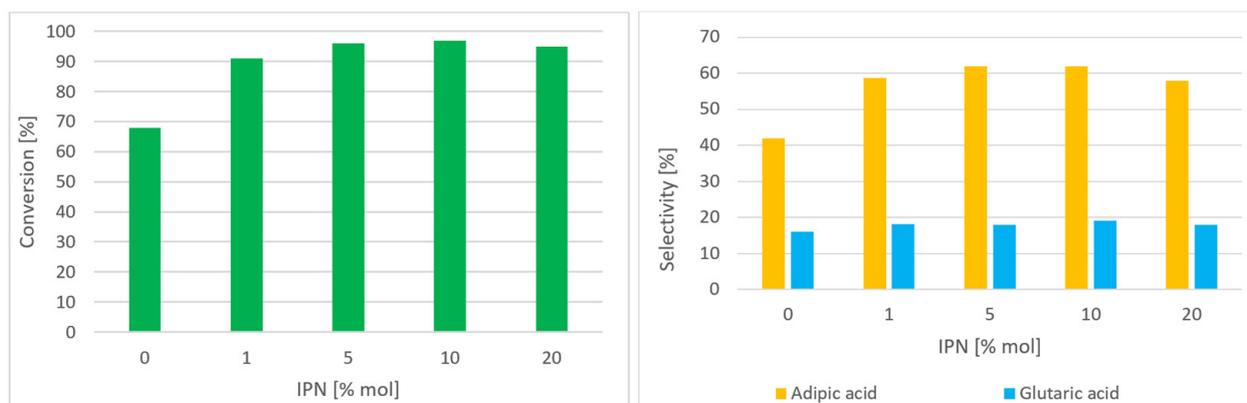


Figure 3. Influence of the amount of IPN on the composition of reaction products C-ON 2 mL (19.3 mmol), AcOH 20 mL (349.7 mmol), IPN 10% mol, Co(acac)₂ 0.5% mol, Mn(acac)₂ 0.5% mol at 60 °C, and oxygen 0.5 MPa at 2 h.

The addition of 1 mol% of IPN increased C-ON conversion from 68% to 91% and AA selectivity from 42% to 59%. When the amount of IPN increased to 5 mol%, AA was obtained in 62% selectivity and 96% conversion. Any further increase in IPN amount (20 mol%) had no significant affect the composition of the reaction products.

Table 3 lists the experimental results examining the influence of temperature, O₂ pressure and the type of solvent on the composition of the products of C-ON oxidation to AA in the IPN/Co²⁺/Mn²⁺ system (Table 3).

Table 3. Influence of selected parameters on the composition of C-ON oxidation reaction products.

Entry	Solvent	Temp. (°C)	Pressure (MPa)	Time (h)	Conv. (%) ^a	Sel. AA (%)	Sel. GA (%)
1	AcOH	40	0.5	2	52	31	10
2	AcOH	50	0.5	2	91	41	11
3	AcOH	60	0.5	2	97	62	19
4	AcOH	80	0.5	2	100	68	18
5	AcOH	100	0.5	2	99	59	21
6 ^b	AcOH	60–80	0.5	2	99	67	23
7	AcOH	60	0.1	2	83	61	17
8	AcOH	60	1.0	2	99	63	21
9	AcOH	60	1.5	2	97	64	21
10 ^c	-	100	0.5	2	35	30	8
11	MeCN	100	0.5	2	99	31	16
12	PhCN	100	0.5	2	99	64	20
13	AcOH	40	0.5	2	52	31	10

C-ON 2 mL (19.3 mmol), solvent 20 mL, IPN 10 mol%, Co(acac)₂ 0.5 mol%, Mn(acac)₂ 0.5 mol%, and O₂ at 2 h; ^a, conversion of C-ON; ^b, 1 h at 60 °C and 1 h at 80 °C; ^c, C-ON 20 mL (193 mmol).

The obtained results showed that as the temperature increased from 40 to 80 °C (entries 1–4), C-ON conversion increased from 52% to 100% and AA selectivity from 31% to 68%. However, when the temperature increased to 100 °C, AA selectivity decreased (entry 5). At higher temperature, the share of the oxidation reaction to by-products such as lower carboxylic acids was greater, as evidenced by the greater selectivity of the GA obtained. The oxidation was carried out at 60 °C for the first 1 h and at 80 °C for the second

h (entry 6). This resulted in similar C-ON conversion and AA selectivity to the reaction conducted at 80 °C (entry 4). Increasing O₂ pressure above 0.1 MPa increased the rate of C-ON oxidation reaction; however, as expected, it did not significantly affect AA selectivity (entries 3, 7–9). According to the results, the role of O₂ was more relevant when considering air or O₂-enriched air oxidation. Elimination of solvent from C-ON oxidation or oxidation conducted in acetonitrile decreased C-ON conversion and significantly decreased AA selectivity (entries 10–12). C-ON oxidation conducted in PhCN gave a conversion of 99% and 64% AA selectivity (entry 13). This approach can be advantageous for industry due to the reduced effect of the reaction medium on the corrosive effect compared to oxidation in AcOH. Hence, the use of PhCN in an industrial process is more desirable due to less corrosion of equipment.

Figure 4 shows the effect of time on C-ON conversion and AA and GA selectivity (1–6 h).

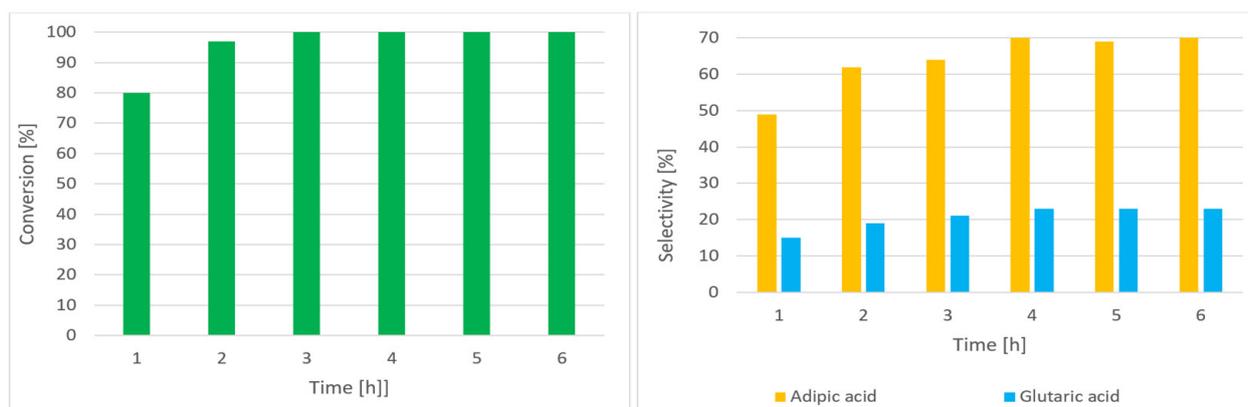


Figure 4. The effect of time on the composition of reaction products C-ON 2 mL (19.3 mmol), AcOH 20 mL (349.7 mmol), IPN 10 mol%, Co(acac)₂ 0.5 mol%, Mn(acac)₂ 0.5 mol% at 60 °C, and O₂ 0.5 MPa.

Under the reaction conditions stated in Figure 4, C-ON conversion was 100% after 3 h. It was found that increasing the reaction time from 1 to 4 h gradually increased AA selectivity from 49% to 71%. Further extension of the reaction time did not affect the composition of the products.

3.2. Oxidation of Cyclohexanol, C-ON, or Their Mixtures with O₂ Using the IPN/Co(acac)₂/Mn(acac)₂ System

As a result of the industrial process of cyclohexane oxidation, a mixture of C-ON and C-OL was formed. Therefore, the possibility of using C-OL or a mixture of C-OL and C-ON in the AA preparation process was investigated in relation to the tested IPN/Co(acac)₂/Mn(acac)₂ system (Table 4).

Table 4. Oxidation of cyclohexanone, cyclohexanol, and cyclohexane.

Entry	Raw Material	Time (h)	Conv. (%) ^a	Sel. AA (%)	Sel. C-ON (%)	Sel. GA (%)
1	C-ON	2	97	62	-	19
2	C-ON	6	100	70	-	23
3	C-OL	2	95	11	47	5
4	C-OL	6	98	20	51	6
5 ^b	C-OL or C-ON	2	100	58	-	17
6 ^b	C-OL or C-ON	6	100	60	-	18

Substrate 2 mL, AcOH 20 mL (349.7 mmol), Co(acac)₂ 0.5 mol%, Mn(acac)₂ 0.5 mol%, IPN 10 mol%, 60 °C, and O₂ 0.5 MPa; ^a, conversion; ^b, retro m:m 1:1.

On the basis of the above results, the main product of the C-OL oxidation reaction was C-ON, and AA was obtained in relatively low selectivity of 11% and 20% after 2 h and 6 h, respectively (entries 3, 4). Using 1:1 (*w:w*) mixture of C-ON and C-OL as the substrate, AA was obtained with 58% selectivity, with 100% conversion of raw materials (entry 5). Prolongation of the oxidation reaction to 6 h only gave a slight increase in AA selectivity (entry 6). It has been reported that the oxidation rate of cyclic alcohol is much lower than that of cyclic ketone, mainly due to the large amounts of C-ON in the mixture used to initiate the oxidation of C-OL to AA.

3.3. Study of the Oxidation of Cyclic Ketones Using the IPN/Co(acac)₂/Mn(acac)₂ System

The possibility of using the proposed catalytic system in the oxidation of a series of cyclic ketones (C₅–C₁₂) in order to form the appropriate dicarboxylic acids (C₅–C₁₂) was examined. The reactions were carried out at 60 °C and 80 °C in the presence and absence of 10 mol% IPN (Table 5).

Table 5. Oxidation of cyclic ketones to dicarboxylic acids.

Entry	Temp. (°C)	IPN (% mol)	Raw Material	Conv. (%) ^a	Sel. Main Product (%)	Sel. By-Product (%)
1	80	-	Cyclopentanone	100	Glutaric acid	Succinic acid
2	80	10		100	33	9
3	60	10		93	47	11
4	60	10		93	20	3
4	80	-	Cyclohexanone	100	Adipic acid	Glutaric acid
5	80	10		100	62	17
6	80	10		100	70	18
6	60	10		100	71	23
7	80	-	Cycloheptanone	87	Pimelic acid	Adipic acid
8	80	10		99	52	15
9	80	10		47	54	18
9	60	10		47	15	3
10	80	-	Cyclooctanone	98	Suberic acid	Pimelic acid
11	80	10		100	62	14
12	80	10		100	70	12
12	60	10		97	54	18
13	80	-	Cyclododecanone	75	Dodecane-1,12-dioic	Undecane-1,11-dioic acid
14	80	10		100	44	10
15	80	10		100	59	9
15	60	10		100	53	3
16	80	-	2-Methyl cyclohexanone	50	6-Oxyheptanoic acid	Glutaric acid
17	80	10		100	44	16
18	80	10		100	68	14
18	60	10		100	69	14
19	80	-	3-Methyl cyclohexanone	69	3-Methyladipic acid	2-Methyladipic acid
20	80	10		100	45	18
21	80	10		100	64	16
21	60	10		100	59	16
22	80	-	4-Methyl cyclohexanone	68	3-Methyladipic acid	2-Methylglutaric acid
23	80	10		100	61	9
24	80	10		100	88	10
24	60	10		99	75	8

Substrate 2 mL, AcOH 20 mL (349.7 mmol), Co(acac)₂ 0.5 mol%, Mn(acac)₂ 0.5 mol%, initiator 10 mol% at 60 °C, and O₂ 0.5 MPa at 2 h; ^a, conversion.

According to the results listed in Table 5, when the temperature was at 80 °C with the addition of 10 mol% IPN, an increase in selectivity was observed for all appropriate dicarboxylic acids. Additionally, the addition of 10 mol% IPN to the oxidation of cycloheptanone, cyclooctanone, cyclododecanone, 2-methylcyclohexanone, 3-methyl cyclohexanone, and 4-methylcyclohexanone increased conversion.

The catalytic activity of the IPN/Co(acac)₂/Mn(acac)₂ system was also productive at 60 °C. Lowering the reaction temperature from 80 °C to 60 °C did not affect the conversion of C-ON (entry 6), cyclododecanone (entry 15), 2-methylcyclohexanone (entry 18), and 3-methylcyclohexanone (entry 21); however, a slight reduction was observed for cyclopentanone (entry 3), cyclooctanone (entry 12), and 4-methylcyclohexanone (entry 24). Furthermore, a noticeable reduction in conversion from 99% to 47% was detected for cycloheptanone. Additionally, reducing the temperature adversely affected the selectivity (entries 3, 9, 12, 15, 24) except for AA (entry 6), 6-oxyheptanoic acid (entry 18), and 3-methyladipic acid (entry 21). The main by-products observed in the reaction were shorter-chain dicarboxylic acids.

3.4. C-ON Oxidation with Air Using the IPN/Co(acac)₂/Mn(acac)₂ System

Industrial oxidation processes using O₂ as an oxidizing agent are associated with a greater risk of explosion due to the formation of a wide range of explosive mixtures between the raw material, solvent, and O₂ compared to air. The oxidation reaction was carried out at a flow of 50 l/h using the IPN/Co²⁺/Mn²⁺ system (Figure 5). Therefore, the oxidation process of C-ON with air and was compared to oxidation using O₂.

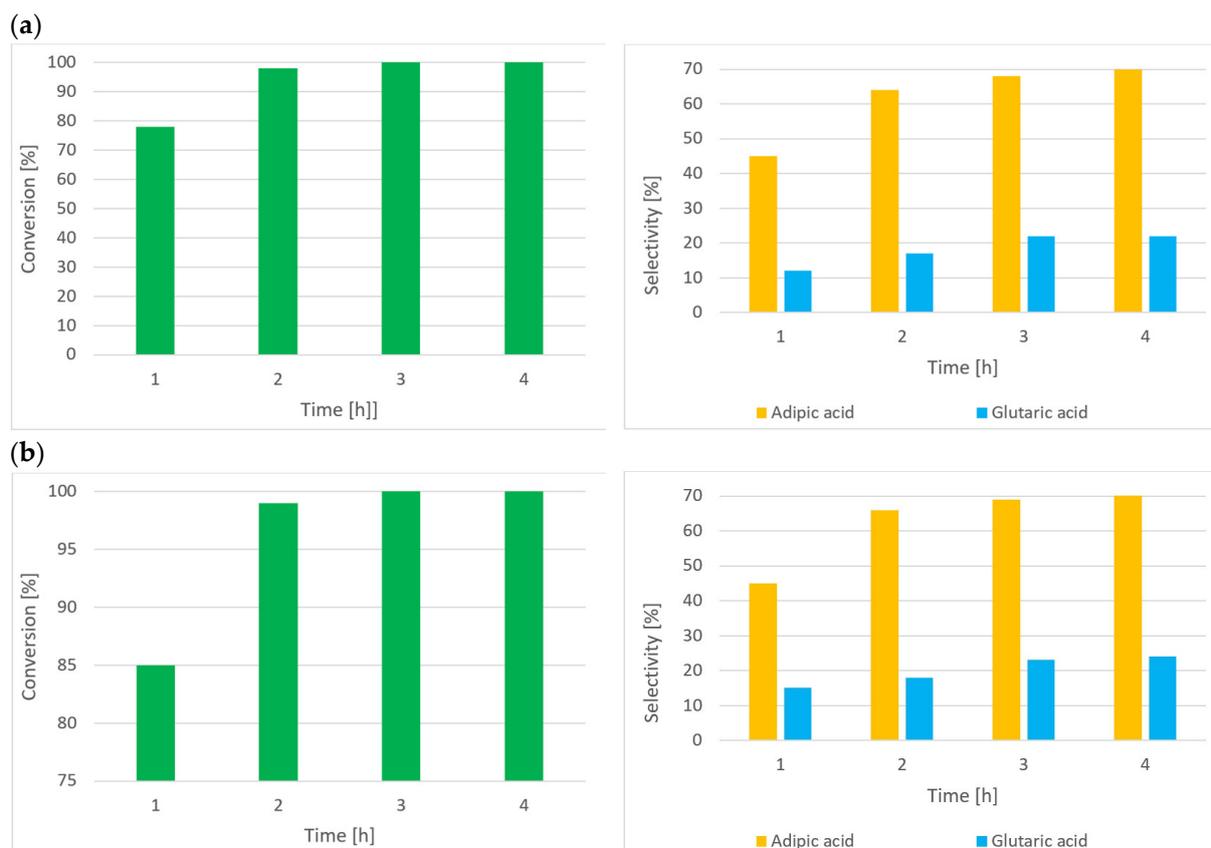


Figure 5. Air or O₂ oxidation of C-ON. C-ON 30 mL (0.29 mol), AcOH 300 mL (5.25 mol), IPN 10 mol%, Co(acac)₂ 0.5 mol%, Mn(acac)₂ 0.5 mol% at 60 °C, and 0.5 MPa. (a) Air 50 l/h; (b) oxygen 50 l/h.

The results showed that under the tested reaction conditions, the type of the oxidizing agent used (air or O₂) had no significant influence on the composition of C-ON oxidation reaction products. However, when the reaction was conducted in O₂, the rate of C-ON

conversion and AA and GA formation was slightly higher after the first 2 h of the reaction. Differences in the reaction rate depended on the oxidizing agent used (air or O₂) and may also have depended on the design of the reactor and distribution system of the oxidizing agent in the liquid reaction mixture.

Figure 6 shows the proposed block diagram of the process for the production of appropriate dicarboxylic acids from cyclic ketones based on our optimized conditions. The figure includes sections for reaction, product isolation and purification, and solvent and catalyst recycling.

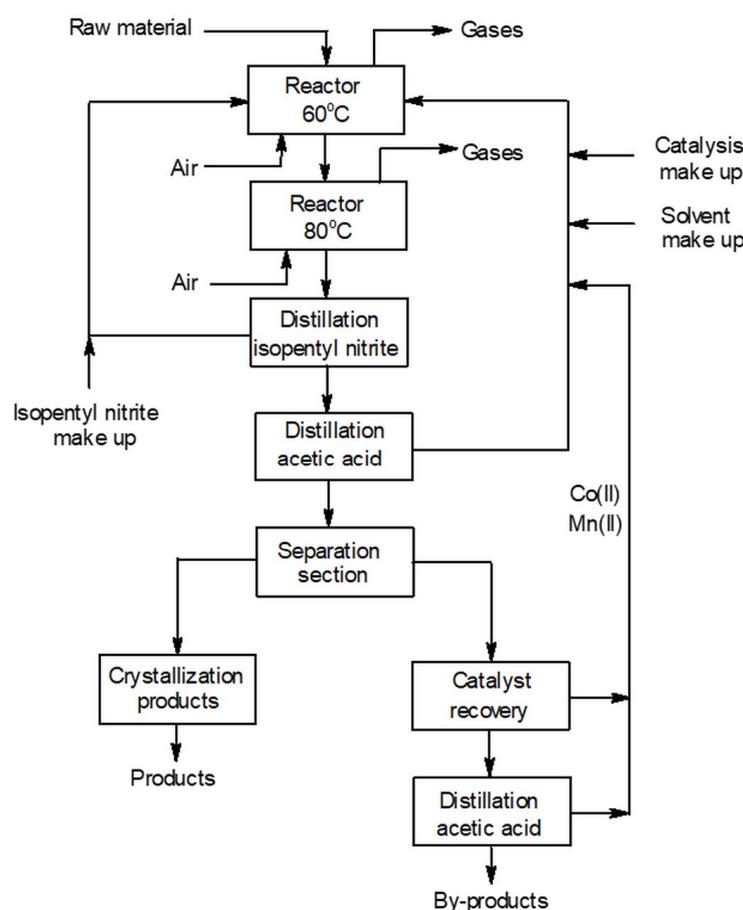


Figure 6. Flowchart for the preparation of carboxylic acids from cyclic ketones.

It is known that the oxidation of cyclic ketones in the presence of O₂ is very exothermic. In the case of 330 mL scale in a 600 mL reactor, it was necessary to cool the reaction mixture in order to maintain a constant temperature. Therefore, a solution to this issue may be the use of a reaction system consisting of a cascade of two reactors. As a result, it was possible to carry out the oxidation at a lower rate in 1one reactor (60 °C), which facilitated the controlled heat removal. The calculated heats of oxidation reactions of C-ON to AA, GA, and SA are 748.9, 1367.3, and 2026.9 kJ/mol, respectively. Taking into account the selectivity of respective reactions (AA = 70%, GA = 22%, SA = 8%) and a 100% conversion of C-ON, the total heat of the oxidation process can be estimated at 987.2 kJ/mol. Our research has shown that the purpose of the second reactor was to increase the selectivity of the reaction via oxygenation of the intermediates. It was therefore advantageous to use a higher temperature of about 80 °C.

The next steps were to separate IPN and part of the solvent (AcOH) from the reaction products. According to the results obtained for the oxidation of C-ON to AA, the concentration of the reaction products by evaporation to approx. 80% AcOH enables separation of AA with 80% efficiency. Upon reduction of the temperature, a precipitate was formed

mainly composed of AA and impurities such as glutaric and succinic acid. AA was further purification by crystallization from AcOH, water, or a mixture thereof. Depending on the type of dicarboxylic acid employed, it was necessary to evaporate different volumes of AcOH due to differences in solubility. The last steps involved the separation and recycling of the Co^{2+} and Mn^{2+} catalyst and the regeneration of residual AcOH.

3.5. Proposed Mechanism for the Oxidation of C-ON with O_2 Using the IPN/ $\text{Co}(\text{acac})_2/\text{Mn}(\text{acac})_2$ System

The current literature has suggested that the addition of alkyl nitrites to the oxidation reaction of cyclic ketones increases the reaction rate, which allows for higher conversions and selectivity at lower temperatures. Figure 7 shows the proposed mechanism of the oxidation of cyclic ketones using the IPN/ $\text{Co}^{2+}/\text{Mn}^{2+}$ system.

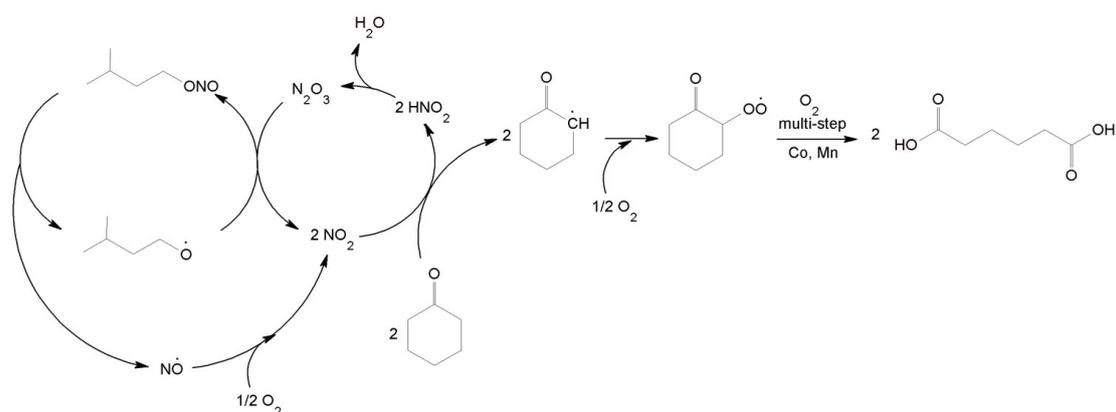


Figure 7. Probable mechanism for the oxidation of C-ON to AA.

We propose that during the reaction, due to temperature, IPN decomposed to isopentyl radical and $\text{NO}\cdot$. $\text{NO}\cdot$ radical was then oxidized to NO_2 under O_2 , which initiated the oxidation of C-ON to form 2-carbonylcyclohexyl radical and HNO_2 . Then, as a result of oxidation, reduction, and disproportionation, the isopentyl radical transformed into IPN [70]. The exact course of AA formation from 2-carbonylcyclohexyl radical was presented in our previous paper [21].

We confirmed the NO_2 catalytic activity by carrying out C-ON oxidation in AcOH, 0.2 mol% $\text{Mn}(\text{acac})_2$, 0.2 mol% $\text{Co}(\text{acac})_2$, and 10 mol% NO_2 (60 °C, air 12 l/h). NO_2 gas produced in a separate reaction vessel by dropping HNO_3 into Cu was redirected to the oxidation reactor along with air. After the brown NO_2 was dissolved in the reaction mixture, a color change was observed from yellow to dark brown as well as O_2 consumption, which was monitored by measuring the O_2 concentration in the gases exiting the reactor. The results showed that the O_2 concentration dropped from 21% to 10% in just 5 min. The reaction continued for a further 2 h.

The water present in the reaction system reacted with NO_2 to form HNO_3 and HNO_2 . The produced HNO_2 molecule completed the catalytic cycle, and the presence of HNO_3 (Table 2, entry 10) influenced the oxidation process. The catalytic activity of HNO_3 in the reaction system was largely related to the pressure. As described earlier, HNO_3 formed an equilibrium with NO_2 , O_2 , and H_2O . Under increased pressure (0.5 MPa), the equilibrium shifted towards HNO_3 , which resulted in lower activity of the $\text{HNO}_3/\text{Co}^{2+}/\text{Mn}^{2+}$ system. However, at atmospheric pressure, the activity of the $\text{HNO}_3/\text{Co}^{2+}/\text{Mn}^{2+}$ system was significantly higher (Figure 8).

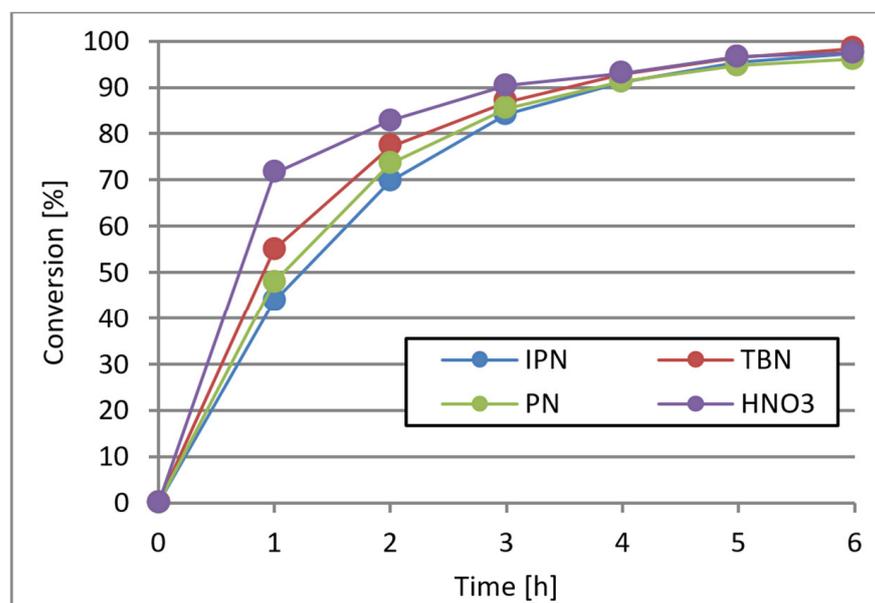


Figure 8. Influence of NO_2 initiator on C-ON conversion at atmospheric pressure. C-ON 8 mL, AcOH 80 mL, $\text{Co}(\text{acac})_2$ 0.2 mol%, $\text{Mn}(\text{acac})_2$ 0.2 mol%, initiator 10 mol%, air 12 l/h, and 0.1 MPa at 60 °C.

Each of the selected catalytic systems was highly active in the C-ON oxidation process. The rate of C-ON oxidation in the presence of HNO_3 was initially faster in comparison to IPN, PN, and TBN. However, it was reduced after 1h. As a result, after 4 h, C-ON conversion was similar in all cases, ranging from 91–92%. After 6 h of reaction, 98% conversion was obtained for all tested catalytic systems.

GC/MS analysis was utilized to confirm the negligible amounts of isopentyl alcohol in the reaction products, which may prove the detachment of the hydrogen atom from the molecule, e.g., C-ON, by the isopentyl radical (Figure 9). A similar mechanism of the catalytic effect of IPN was proposed by researchers when examining the oxidation of cyclohexane directly to AA⁵⁵. The isopentyl radical removes the hydrogen atom from cyclohexane, producing cyclohexyl radical and isopentyl alcohol, which, as a result of slow conversion, generates IPN via the reaction with HNO_2 . Interestingly, only small amounts of isopentyl alcohol were observed in our reaction products even when they were conducted using 20 mol% IPN. Therefore, only slight conversion of IPN to alcohol occurs under the proposed reaction conditions.

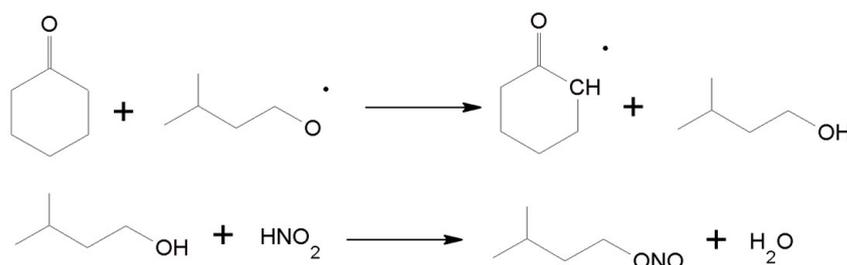


Figure 9. Removal of the hydrogen atom from C-ON via isopentyl radical.

Additionally, it may be also possible to detach the hydrogen atom from C-ON via radical $\text{NO}\cdot$ to form 2-carbonylcyclohexyl radical and HNO . The presence of HNO in the reaction system could promote N_2O formation as a by-product. Reports have shown that HNO can undergo dimerization to form N_2O and H_2O or react with the NO_2 present in the system, which generates NO and HNO_2 . However, the possible reactions leading to N_2O were insignificant due to the low probability of HNO formation in the highly oxidizing

reaction medium. Moreover, HNO dimerization was unlikely due to its trace amounts in the reaction system.

4. Conclusions

Herein, we found a positive effect of the addition of IPN, TBN, PN, and HNO₃ towards the composition of the products resulting from C-ON oxidation to AA in air. In the presence of the IPN/Co²⁺/Mn²⁺ catalytic system, AA was obtained in the highest selectivity. Additionally, the anion type in the salt as well as the Co²⁺ and Mn²⁺ complexes did not affect the composition of the reaction products. Through examination of selected parameters, it was revealed that the C-ON oxidation reaction for 4 h at 60 °C was satisfactory, producing AA with 71% selectivity and 100% C-ON conversion. A similar effect was observed when the reaction was conducted for 2 h at 60 °C and then for an additional 2 h at 80 °C. This approach was more advantageous for industrial processes due to dispersion of potentially hazardous energy. Shorter-chain acids, mainly GA and BA, were observed as the main by-products.

The developed catalytic system IPN/Co(acac)₂/Mn(acac)₂ successfully increased the selectivity of dicarboxylic acids determined from cyclic ketones. The type of oxidizing agent used (air or O₂) did not affect the composition of the reaction products. However, on a larger scale, it was necessary to carry out the oxidation reaction in air due to safety reasons. The results indicate that the oxidation proceeds with a high energy effect, which requires a reactor with efficient cooling.

A block diagram was presented describing the preparation of dicarboxylic acids as a simple method requiring only a limited number of unit operations. The raw materials, solvents, and catalysts used were commercially available, and their prices were relatively low. The proposed method for the obtainment of AA from C-ON, using air as the oxidizing agent, was more environmentally friendly than other industrial methods, which employ HNO₃ as an oxidant.

It is highly probable that in the next 5–10 years, the use of HNO₃ as an oxidizing agent will no longer be necessary. The market report [71] for AA for 2020–2025 clearly emphasizes the expectations of stringent environmental regulations regarding the production process. These regulations are likely to inhibit market development and increase interest in technologies for the AA production, e.g., bio-based. It is estimated that new technologies will be implemented in the coming years. The chemical industry recognizes this threat and therefore conducts intensive research to improve the existing production methods or select new alternative production methods.

The proposed method for AA production is an interesting alternative to current industrial production methods based on HNO₃. Certainly, the optimization of C-ON oxidation using the Co/Mn/IPN system can increase selectivity, which has economic benefits. Moreover, legal and environmental conditions related to the emission of greenhouse gases significantly influence the constantly growing price of AA on the world markets. Therefore, it is possible that current technologies for dicarboxylic acids formation may be considered unprofitable in the future and our method an interesting alternative to the traditional, non-ecological method.

5. Patents

The research results described in this article have become the subject of a Polish patent with the number PL 239347.

Author Contributions: Conceptualization, D.L. and B.O.; methodology, D.L., B.O., K.D., J.B. and T.M.; Software, D.L.; Formal analysis, D.L.; Investigation, D.L.; Resources, D.L.; Writing—original draft, D.L.; Writing—review & editing, D.L.; Visualization, D.L.; Supervision, B.O.; Funding acquisition: D.L., B.O., T.M. and K.D. All authors have read and agreed to the published version of the manuscript.

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References

1. Rios, J.; Lebeau, J.; Yang, T.; Li, S.; Lynch, M.D. A critical review on the progress and challenges to a more sustainable, cost competitive synthesis of adipic acid. *Green Chem.* **2021**, *23*, 3172–3190.
2. Lisicki, D.; Orlińska, B. Oxidation of cyclic ketones to dicarboxylic acids. *Pol. J. Chem. Tech.* **2018**, *20*, 102–107.
3. Cornils, B.; Lappe, P. Dicarboxylic acids, aliphatic. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2005.
4. Research and Markets. The World's Largest Market Research Store. Available online: www.researchandmarkets.com/reports/3641969/global-markets-for-adipic-acid#relc2 (accessed on 30 June 2023).
5. Lisicki, D.; Dobras, G.; Orlińska, B.; Zawadiak, J. Metody otrzymywania kwasu adypinowego o potencjalnym zastosowaniu przemysłowym. *Przem. Chem.* **2017**, *96*, 1485–1489.
6. Abutaleb, A.; Ali, M.A. A comprehensive and updated review of studies on the oxidation of cyclohexane to produce ketone-alcohol (KA) oil. *Rev. Chem. Eng.* **2021**, *38*, 769–797.
7. Li, G.; Liu, S.; Dou, X.; Wei, H.; Shang, M.; Luo, Z.H.; Su, Y. Synthesis of Adipic Acid through Oxidation of K/A oil and Its Kinetic Study in a Microreactor System. *Reaction Engineering. AIChE J.* **2020**, *66*, e16289.
8. Musser, M.T. Adipic acid. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2012.
9. UN Environment Programme. Drawing down N2O to Protect Climate and the Ozone Layer a UNEP Synthesis Report. Available online: <https://wedocs.unep.org/handle/20.500.11822/8489> (accessed on 30 June 2023).
10. Task Force on National Greenhouse Gas Inventories. Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories, Chapter 3 Industrial Processes. Available online: <https://www.ipcc-nggip.iges.or.jp/public/gp/english/8489> (accessed on 30 June 2023).
11. Artz, J.; Palkovits, S.; Palkovits, R.; Creusen, G.; Holzha, F.J. Producing Widespread Monomers from Biomass Using Economical Carbon and Ruthenium—Titanium Dioxide Electrocatalysts. *ACS Sustain. Chem. Eng.* **2018**, *6*, 17108–17113.
12. Hatakeyama, K.; Nakagawa, Y.; Tamura, M.; Tomishige, K. Efficient production of adipic acid from 2-methoxycyclohexanone by aerobic oxidation with a phosphotungstic acid catalyst. *Green Chem.* **2020**, *22*, 4962–4974.
13. Corona, A.; Bidy, M.J.; Vardon, D.R.; Birkved, M.; Hauschild, M.Z.; Beckham, G.T. Life cycle assessment of adipic acid production from lignin. *Green Chem.* **2018**, *20*, 3857–3866.
14. Pyo, S.H.; Park, J.H.; Srebny, B.; Hatti-Kaul, R. A sustainable synthetic route for biobased 6-hydroxyhexanoic acid, adipic acid and ϵ -caprolactone by integrating bio- and chemical catalysis. *Green Chem.* **2020**, *22*, 4450.
15. Rauen, A.L.; Weinelt, F.; Waldvogel, S.R. Sustainable electroorganic synthesis of lignin-derived dicarboxylic acids. *Green Chem.* **2020**, *22*, 5956–5960.
16. Pellis, A.; Byrne, F.P.; Sherwood, J.; Vastano, M.; Comerford, J.W.; Farmer, T.J. Safer bio-based solvents to replace toluene and tetrahydrofuran for the biocatalyzed synthesis of polyesters. *Green Chem.* **2019**, *21*, 1686–1694.
17. Montazeri, M.; Zaimes, G.G.; Khanna, V.; Eckelman, M.J. Meta-Analysis of Life Cycle Energy and Greenhouse Gas Emissions for Priority Biobased Chemicals. *ACS Sustain. Chem. Eng.* **2016**, *4*, 6443–6454.
18. Hwang, K.C.; Sagadevan, A. One-pot room-temperature conversion of cyclohexane to adipic acid by ozone and UV light. *Science* **2014**, *346*, 1495–1498.
19. Matsumoto, Y.; Kuriyama, M.; Yamamoto, K.; Nashida, K.; Onomura, O. Metal-free synthesis of adipic acid via organocatalytic direct oxidation of cyclohexane under ambient temperature and pressure. *Org. Process. Res. Dev.* **2018**, *22*, 1312–1317.
20. Rao, D.G.; Tirukkoyllur, R.S. Liquid-phase oxidation of cyclohexane to adipic acid in a single stage. *Ind. Eng. Chem. Process Des. Dev.* **1986**, *25*, 299–304.
21. Lisicki, D.; Orlińska, B.; Marek, A.A.; Bińczak, J.; Dziuba, K.; Martyniuk, T. Oxidation of Cyclohexane/Cyclohexanone Mixture with Oxygen as Alternative Method of Adipic Acid Synthesis. *Materials* **2023**, *16*, 298.
22. Kulsrestha, G.N.; Saxena, M.P.; Gupta, A.K.; Goyal, H.B.; Prasad, R.; Prasad, R.T.S.R.; Patel, P.D. Catalyst and a Process for Preparing Carboxylic Acids Using the Catalyst. U.S. Patent US5547905, 20 August 1996.
23. Liang, F.; Zhong, W.; Xiang, L.; Mao, L.; Xu, Q.; Kirk, S.R.; Yin, D. Synergistic hydrogen atom transfer with the active role of solvent: Preferred one-step aerobic oxidation of cyclohexane to adipic acid by *N*-hydroxyphthalimide. *J. Catal.* **2019**, *378*, 256–269.

24. Ishii, Y.; Iwahama, T.; Sakaguchi, S.; Nakayama, K.; Nishiyama, Y. Alkane oxidation with molecular oxygen using a new efficient catalytic system: *N*-hydroxyphthalimide (NHPI) Combined with $\text{Co}(\text{acac})_n$ ($n = 2$ or 3). *J. Org. Chem.* **1996**, *61*, 4520–4526.
25. Ishii, Y. A novel catalysis of *N*-hydroxyphthalimide (NHPI) combined with $\text{Co}(\text{acac})_n$ ($n=2$ or 3) in the oxidation of organic substrates with molecular oxygen. *J. Mol. Catal. A Chem.* **1997**, *117*, 123–137.
26. Iwahama, T.; Syojo, K.; Sakaguchi, S.; Ishii, Y. Direct conversion of cyclohexane into adipic acid with molecular oxygen catalyzed by *N*-hydroxyphthalimide combined with $\text{Mn}(\text{acac})_2$ and $\text{Co}(\text{OAc})_2$. *Org. Process Res. Dev.* **1998**, *2*, 255–260.
27. Ishii, Y.; Sakaguchi, S. A new strategy for alkane oxidation with O_2 using *N*-hydroxyphthalimide (NHPI) as a radical catalyst. *Catal. Surv. Jpn.* **1999**, *3*, 27–35.
28. Ishii, Y.; Sakaguchi, S.; Iwahama, T. Innovation of hydrocarbon oxidation with molecular oxygen and Related Reactions. *Adv. Synth. Catal.* **2001**, *343*, 393–427.
29. Ishii, Y.; Sakaguchi, S. Recent progress in aerobic oxidation of hydrocarbons by *N*-hydroxyimides. *Catal. Today* **2006**, *117*, 105–113.
30. Schulz, J.G.D.; Onopchenko, A. Process for Converting Cyclohexane to Adipic Acid. U.S. Patent US4263453, 21 April 1981.
31. Thomas, J.M.; Raja, R. Catalytically active centres in porous oxides: Design and performance of highly selective new catalysts. *Chem. Commun.* **2001**, *8*, 675–687.
32. Mikami, Y.; Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. Superior performance of Fe(BTC) with respect to other metal-containing solids in the *N*-hydroxyphthalimide-promoted heterogeneous aerobic oxidation of cycloalkanes. *ChemCatChem* **2013**, *5*, 1964–1970.
33. Yuan, Y.; Ji, H.; Chen, Y.; Han, Y.; Song, X.; She, Y.; Zhong, R. Oxidation of cyclohexane to adipic acid using Fe-porphyrin as a biomimetic catalyst. *Org. Process Res. Dev.* **2004**, *8*, 418–420.
34. Sawatari, N.; Yokota, T.; Sakaguchi, S.; Ishii, Y. Alkane oxidation with air catalyzed by lipophilic *N*-hydroxyphthalimides without any solvent. *J. Org. Chem.* **2001**, *66*, 7889–7891.
35. Chavan, S.A.; Srinivas, D.; Ratnasamy, P. Oxidation of cyclohexane, cyclohexanone, and cyclohexanol to adipic acid by a non- HNO_3 Route over Co/Mn cluster complexes. *J. Catal.* **2002**, *212*, 39–45.
36. Wang, T.; She, Y.; Fu, H.; Li, H. Selective cyclohexane oxidation catalyzed by manganese porphyrins and co-catalysts. *Catal. Today* **2016**, *264*, 3–8.
37. Kerry Yu, K.M.; Abutaki, A.; Zhou, Y.; Yue, B.; He, H.Y.; Tsang, S.C. Selective oxidation of cyclohexane in supercritical carbon dioxide. *Catal Lett.* **2007**, *113*, 115–119.
38. Kamath, S.S.; Chandalia, S.B. Liquid phase oxidation of cyclohexanone to adipic acid by air in acetic acid solution. *J. Appl. Chem. Biotechnol.* **1973**, *23*, 469–478.
39. Flemming, W.; Speer, W. Catalytic Oxidation of Ketones. U.S. Patent US2005183, 18 June 1935.
40. Flemming, W. Catalytic Oxidation of Ketones. U.S. Patent US2299013, 13 October 1942.
41. Flemming, W. Production of Dibasic Acids. U.S. Patent US2452741, 2 November 1948.
42. Dassel, M.W.; Decoster, D.C.; Rostami, A.M.; Aldrich, S.M.; Vassiliou, E. Methods for Preparing Dibasic Acids. U.S. Patent US5922908, 13 July 1999.
43. Longley, K.D.; Sprowl, D. Process of Producing Adipic Acid. U.S. Patent US3869508, 4 March 1975.
44. Zou, G.; Zhong, W.; Mao, L.; Xu, Q.; Xiao, J.; Yin, D.; Xiao, Z.; Kirk, S.R.; Shu, T. 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.* **2015**, *17*, 1884–1892.
45. Besson, M.; Gauthard, F.; Horvath, B.; Gallezot, P. Catalytic oxidation with air of cyclohexanone to dicarboxylic acids on synthetic carbons. Effect of supported metals and solvents. *J. Phys. Chem. B* **2005**, *109*, 2461–2467.
46. Crezee, E.; Barendregt, A.; Kapteijn, F.; Moulijn, J. Carbon coated monolithic catalysts in the selective oxidation of cyclohexanone. *Catal. Today* **2001**, *69*, 283–290.
47. Pigamo, A.; Besson, M.; Black, B.; Gallezot, P.; Blackburn, A.; Kozynchenko, O.; Tennison, S.; Crezee, E.; Kapteijn, F. Effect of oxygen functional groups on synthetic carbons on liquid phase oxidation of cyclohexanone. *Carbon* **2002**, *40*, 1267–1278.
48. Bhanja, P.; Ghosh, K.; Islam, S.S.; Patra, A.K.; Islam, S.M.; Bhaumik, A. New Hybrid Iron Phosphonate Material as an Efficient Catalyst for the Synthesis of Adipic Acid in Air and Water. *ACS Sustain. Chem. Eng.* **2016**, *4*, 7147–7157.
49. Shen, H.C.; Weng, H.S. Liquid-phase oxidation of cyclohexane to dibasic acids with immobilized cobalt catalyst. *Ind. Eng. Chem. Res.* **1988**, *27*, 2254–2260.
50. Rae, D.G.; Raghunathan, T.S. Oxidation of cyclohexanone to adipic acid with a cobalt acetate/oxygen/acetic acid system. *J. Chem. Technol. Biotechnol. Chem. Technol.* **1984**, *34*, 381–386.
51. Cavani, F.; Ferroni, L.; Frattini, A.; Lucarelli, C.; Mazzini, A.; Raabova, K.; Alini, S.; Accorinti, P.; Babini, P. Evidence for the presence of alternative mechanisms in the oxidation of cyclohexanone to adipic acid with oxygen, catalysed by Keggin polyoxometalates. *Appl. Catal. A Gen.* **2011**, *391*, 118–124.
52. Atlamsani, A.; Brégeault, J.M.; Ziyad, M. Oxidation of 2-methylcyclohexanone and cyclohexanone by dioxygen catalyzed by vanadium-containing heteropolyanions. *J. Org. Chem.* **1993**, *58*, 5663–5665.
53. Shimizu, A.; Tanaka, K.; Ogawa, H.; Matsuoka, Y.; Fujimori, M.; Nagamori, Y.; Hamachi, H.; Kimura, K. An industrial process for adipic acid production by the liquid-phase oxidation of cyclohexanone with molecular oxygen. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1991–2001.
54. Jie, X.; Xiuquan, J.; Jiping, M.; Xiaofang, L.; Jin, G.; Yong-Ming, X.; Fei, X. Method for Preparation of Adipic Acid by Oxidizing Cyclohexanone. C.N. Patent CN108084012, 25 May 2018.

55. She, M.; Gu, R.; Meng, D.; Yang, H.; Wen, Y.; Qian, X.; Guo, X.; Dang, W. Nanosheets of Ni-SAPO-34 Molecular Sieve for Selective Oxidation of Cyclohexanone to Adipic Acid. *Chem. Eur. J.* **2022**, *28*, e202200696.
56. Suzuki, Y.; Harada, E.; Nakamaru, K.; Takeda, Y.; Sano, M.; Hashimoto, K.; Miyake, T. Direct oxidation of cycloalkanes with molecular oxygen to dicarboxylic acids using isoamyl nitrite. *J. Mol. Catal. A Chem.* **2007**, *276*, 1–7.
57. Ning, X.; Wang, M.; Yao, C.; Chen, X.; Kang, Y. *tert*-Butyl Nitrite: Organic Redox Cocatalyst for Aerobic Aldehyde-Selective Wacker—Tsuji Oxidation. *Org. Lett.* **2016**, *18*, 2700–2703.
58. Hu, K.; Ning, X.; Qu, J.; Kang, Y. Tuning Regioselectivity of Wacker Oxidation in One Catalytic System: Small Change Makes Big Step. *J. Org. Chem.* **2018**, *83*, 11327–11332.
59. Links, D.A. Green Chemistry *Tert*-butyl nitrite: A metal-free radical initiator for aerobic cleavage of benzylic C=C bonds in compressed carbon dioxide†. *Green Chem.* **2011**, *13*, 541–544.
60. Shen, Z.; Dai, J.; Xiong, J.; He, X.; Mo, W.; Hu, B. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)/*tert*-Butyl Nitrite/Oxygen: A Versatile Catalytic Oxidation System. *Adv. Synth. Catal.* **2011**, *353*, 3031–3038.
61. Xie, Y.; Mo, W.; Xu, D.; Shen, Z.; Sun, N.; Hu, B.; Hu, X. Efficient NO Equivalent for Activation of Molecular Oxygen and Its Applications in Transition-Metal-Free Catalytic Aerobic Alcohol Oxidation alcohol oxidation. *J. Org. Chem.* **2007**, *72*, 4288–4291.
62. He, X.; Shen, Z.; Mo, W.; Sun, N.; Hu, B. TEMPO-*tert*-Butyl Nitrite: An Efficient Catalytic System for Aerobic Oxidation of Alcohols. *Adv. Synth. Catal.* **2009**, *351*, 89–92.
63. Dong, Y.; Zhao, X.; Liu, R. 4-OH-TEMPO/TCQ/TBN/HCl: A Metal-Free Catalytic System for Aerobic Oxidation of Alcohols under Mild Conditions. *Chin. J. Chem.* **2015**, *33*, 1019–1023.
64. Karimi, B.; Farhangi, E. A Highly Recyclable Magnetic Core-Shell Nanoparticle-Supported TEMPO catalyst for Efficient Metal- and Halogen-Free Aerobic Oxidation of Alcohols in Water. *Chem. Eur. J.* **2011**, *17*, 6056–6060.
65. Links, D.A. SBA-15-functionalized TEMPO confined ionic liquid: An efficient catalyst system for transition-metal-free aerobic oxidation of alcohols with improved selectivity. *Org. Biomol. Chem.* **2011**, *9*, 4194–4198.
66. Walsh, K.; Sneddon, H.F.; Moody, C.J. Solar Photochemical Oxidations of Benzylic and Allylic Alcohols Using Catalytic Organooxidation with DDQ: Application to Lignin Models. *Org. Lett.* **2014**, *16*, 5224–5227.
67. Ma, J.; Hong, C.; Wan, Y.; Li, M.; Hu, X.; Mo, W.; Hu, B.; Sun, N.; Jin, L.; Shen, Z. Aerobic oxidation of secondary alcohols in water with ABNO/*tert*-butyl nitrite/KPF 6 catalytic system. *Tetrahedron Lett.* **2017**, *58*, 652–657.
68. Hu, Y.; Chen, L.; Li, B. NHPI/*tert*-butyl nitrite: A highly efficient metal-free catalytic system for aerobic oxidation of alcohols to carbonyl compounds using molecular oxygen as the terminal oxidant. *Catal. Commun.* **2016**, *83*, 82–87.
69. Shibuya, M.; Furukawa, K.; Yamamoto, Y. Selective Aerobic Oxidation of Primary Alcohols to Aldehydes. *Synlett* **2017**, *28*, 1554–1557.
70. Gunchenko, P.A.; Li, J.; Liu, B.; Chen, H.; Pashenko, A.E.; Bakhonsky, V.V.; Zhuk, T.S.; Fokin, A.A. Aerobic oxidations with *N*-hydroxyphthalimide in trifluoroacetic acid. *Mol. Catal.* **2018**, *447*, 72–79.
71. Market Research Future. Available online: <https://www.marketresearchfuture.com/reports/adipic-acid-market-5479> (accessed on 30 June 2023).

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