Direct oxidation of cycloalkanes with molecular oxygen to dicarboxylic acids using isoamyl nitrite

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Abstract

Oxidation of cycloalkanes with molecular oxygen using isoamyl nitrite was examined under mild conditions. Cycloalkanes were easily oxidized with molecular oxygen to give the corresponding cycloalcohols, cycloalkanones and dicarboxylic acids at 120 °C or lower temperatures. The oxidation of the cycloalkanes was promoted by adding soluble Co and Mn ions.
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Keywords: Isoamyl nitrite; Oxidation; Cyclohexane; Adipic acid

1. Introduction

Adipic acid, which is one of the most important commodity chemicals in the modern chemical industry as, for example, a raw material for nylon 66, is manufactured by the oxidation of cyclohexanone obtained either by hydrogenation of phenol or more commonly by oxidation of cyclohexane [1]. About 2.3 million tonnes per year of adipic acid are produced all over the world nowadays [2]. Most of industrial manufacturing processes apply the two-step method [3]. The first step is oxidation of cyclohexane to cyclohexanone/cyclohexanol (K/A oil) with air in the presence of Co salt catalyst. It is necessary to conduct the first step under air at high temperature of about 150–170 °C. Moreover, because it is necessary to suppress the conversion of cyclohexane to 3–5% to reduce formation of by-products, much energy is needed to recycle un-reacted cyclohexane. Therefore, strenuous efforts have been exerted to improve this step [4]. Direct oxidation of cyclohexane to adipic acid using a higher concentration of Co salt is also reported [5,6], however, favorable results are not obtained so far. The second step is oxidation of cyclohexanone/cyclohexanol to adipic acid with nitric acid [7]. In this step, a large amount of nitrous oxide (N_2O) is generated and vented, causing environmental pollution [8–10]. The amount of N_2O generated globally is estimated to be 26 million tonnes per year [11] and the concentration of N_2O in the atmosphere is increasing at the rate of 0.2% per year [12,13].

From the environmental viewpoint, oxidation with molecular oxygen is more attractive and preferable, because it produces no N_2O. Recently, oxidation reactions with oxygen using *N*-hydroxyphthalimide radical as a catalyst were reported [14–16].

From these backgrounds, therefore, the direct oxidation of cyclohexane to adipic acid under mild reaction conditions is industrially awaited. In this paper, we report that by selecting promoters adipic acid can be obtained with high selectivity from cyclohexane under mild reaction conditions using isoamyl nitrite.

2. Experimental

Reaction was carried out in a 50 cm^3 stainless steel autoclave at 120 °C for 6 h and the initial oxygen pressure was 0.91 MPa. Typically, cyclohexane 5.39 g (64 mmol), isoamyl nitrite 0.38 g (3.2 mmol) as alkyl nitrite, Co(III) acetylacetonate (Co(acac)$_3$) 9.4 mg (26.4 μmol) and Mn(III) acetylacetonate (Mn(acac)$_3$) 9.3 mg (26.4 μmol) were introduced into the autoclave. Purchased reagents from Wako Pure Chemical Industries, Ltd. were used as received. Labeled purity of cyclohexane was 99.8% and

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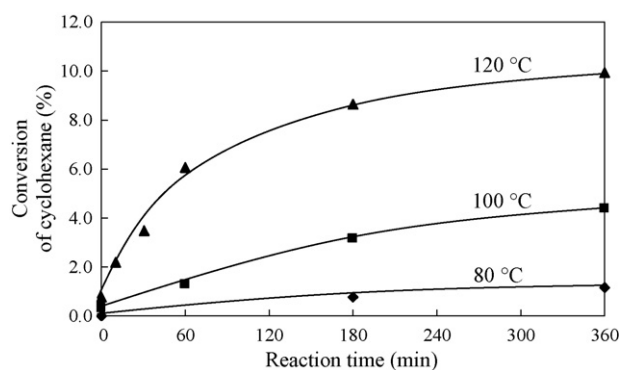 *E-mail address:* tmiyake@ipcku.kansai-u.ac.jp (T. Miyake).

Fig. 1. Influence of reaction temperature upon conversion of cyclohexane. Cyclohexane 64 mmol, isoamyl nitrite 5 mol%, $Co(acac)_3$ 0.04 mol% and P_{O_2} 0.91 MPa.

Fig. 2. Influence of reaction temperature upon amount of estimated oxygen consumption. Cyclohexane 64 mmol, isoamyl nitrite 5 mol%, $Co(acac)_3$ 0.04 mol% and P_{O_2} 0.91 MPa.

our GC analysis indicated that the amounts of cyclohexanol and cyclohexanone were below the detection limit with only trace amounts of saturated hydrocarbons detected. After purge of air with nitrogen, the autoclave was pressurized with oxygen to 0.8 MPa. Then, the temperature was raised to 120 °C and then total pressure was raised to 1.1 MPa with oxygen. As an autogeneous pressure of cyclohexane is 0.19 MPa, the actual initial oxygen pressure is 0.91 MPa.

The products except adipic acid were analyzed by gas chromatography (Shimadzu; GC-8A, FID). A glass column of 3.2 mm width and 2.0 m length packed with polystyrene-divinylbenzene polymer (Gaskuropak 55) was used and the internal standard method was adopted (internal standard: cyclopentanol). The amount of adipic acid was measured by neutralization titration. To check the formation of other acids such as glutaric acid and succinic acid, an aliquot of the reaction mixture (3 g) was esterified with methanol (30 cm^3) in the presence of three drops of concentrated H_2SO_4 at 50 °C for 6 h. From GC analysis, no detectable amounts of esters of other acids than adipic acid were found [17,18]. Selectivities of products (C_6-basis) were calculated based on the summed amount of products from GC analysis and the neutralization titration. Carbon-based material balance was higher than 95% except a few cases (93%).

3. Results and discussion

Figs. 1 and 2 show the influence of reaction temperature upon the conversion of cyclohexane and estimated oxygen consumption based on pressure decrease, respectively. At lower reaction temperature, conversion increased linearly with time and the estimated oxygen consumption rate was almost constant. On the other hand, at 120 °C the reaction rate increased notably and after 60 min it decreased gradually. A high cyclohexane conversion of about 10% was attained after 3 h. Interestingly, fast and constant oxygen consumption was observed till 60 min and even thereafter oxygen was consumed constantly (Fig. 2). This suggests that consumed oxygen during initial 60 min is directly related to the oxidation of cyclohexane and at the latter stage is used for oxidation of primary products. The oxygen consumption was estimated based on the pressure decrease, which does not give precise oxygen consumption because of possible contri-
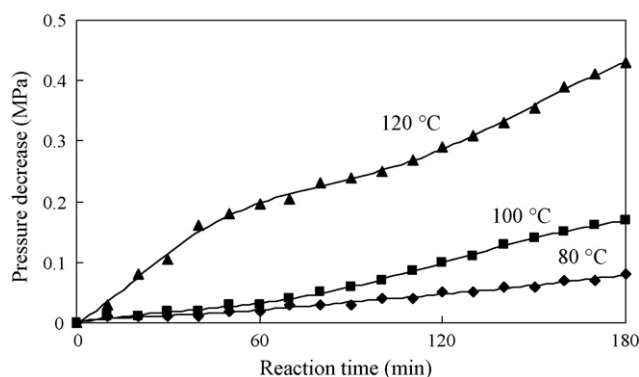
bution of, for example, partial pressures of H_2O and NO_2 formed during the reaction. We calculated material balance of oxygen for Run 5 at 95% assuming NO_2 formation.

Fig. 3 shows the selectivity change during the reaction at 120 °C for 6 h. At the very early stage of the reaction, cyclohexanol and adipic acid (AA) were the main products and the selectivity for cyclohexanone was very low. As the reactivity of cyclohexanone is higher than that of cyclohexane, once formed cyclohexanone was quickly converted to the final and desired product, AA. As time proceeded, the selectivity for cyclohexanone increased at the expense of cyclohexanol. Considering the results shown in Figs. 1 and 2, the reaction mechanism will be discussed later in detail together with other useful data obtained. As the favorable data was obtained at 120 °C and for 3 h, these conditions were adopted for the following experiments.

To improve the cyclohexane conversion and AA selectivity, promoters were added and the result is shown in Table 1. Here we chose Co and Mn ions, because these ions are very often used as liquid-phase oxidation catalysts [19–21]. Even a small amount of $Co(acac)_3$ or $Mn(acac)_3$ catalyzed the reaction, however, the selectivity for AA was lower than 20%. When isoamyl nitrite was combined with $Co(acac)_3$ and $Mn(acac)_3$, the conversion increased to about 10% and it should be stressed that the selectivity for AA increased drastically to 35%.

Fig. 4 shows the Arrhenius plot for oxidation of cyclohexane. The apparent activation energy was calculated from the
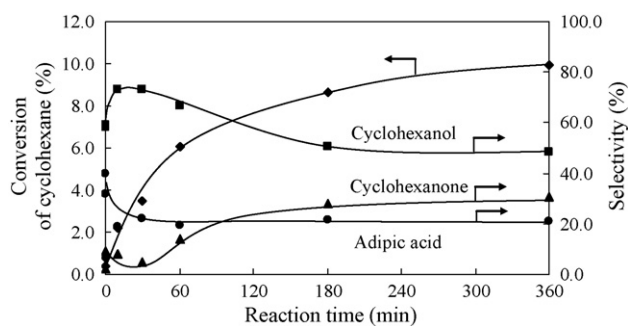

Fig. 3. Influence of reaction time upon product distribution. Cyclohexane 64 mmol, isoamyl nitrite 5 mol%, $Co(acac)_3$ 0.04 mol%, 120 °C and P_{O_2} 0.91 MPa.

Table 1
Influence of catalyst system upon oxidation of cyclohexane

Run no.	Isoamyl nitrite (mol%)	Co(acac)$_3$ (mol%)	Mn(acac)$_3$ (mol%)	Conversion (%)	Selectivity (%)		
					Cyclohexanol	Cyclohexanone	Adipic acid
1	5	–	–	6.7	58.4	18.9	22.7
2	–	0.04	–	3.8	47.9	36.2	15.9
3	–	–	0.04	1.0	59.6	21.8	18.6
4	5	0.04	–	8.6	50.8	27.8	21.4
5	5	0.04	0.04	9.7	52.7	11.9	35.4

Cyclohexane 64 mmol, 120 °C, P_{O_2} 0.91 MPa and 3 h.

straight line at 107 kJ mol^{-1}. The activation energy of *t*-butyl nitrite decomposition is reported to be 29 kJ mol^{-1} [22]. On the other hand, the activation energies for cyclohexane oxidation on CoAPO-5 [23] and cobalt-type weak acid resin [24] are reported to be 167 and 86 kJ mol^{-1}, respectively. Considering these activation energies, the rate-determining step of this reaction is not the decomposition of isoamyl nitrite but the dissociation of the C–H bond of cyclohexane.

Influence of the amount of catalysts and kinds of manganese promoter is shown in Table 2. First, the effect of the main component, isoamyl nitrite,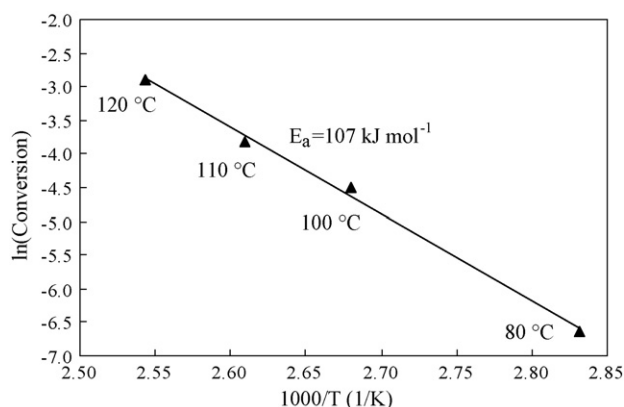 with constant amount of the other Co and Mn promoters can be seen from Runs 5 to 8. The conversion increased proportionally with increasing amount of isoamyl nitrite up to 5 mol%. However, when the amount of isoamyl nitrite was increased further, the conversion of cyclohexane decreased (Run 8). This may be explained by assuming coupling of radicals formed by decomposition of isoamyl nitrite or intermediate radical species. The kinds of manganese promoter seem to have minor influence on the oxidation of cyclohexane (Runs 5, 9–11). Manganese promoters of various valences gave similar results and this may indicate that under the reaction conditions adopted the valence of manganese may have changed to the same one. Here, it should be noted that high AA selectivity, almost 40%, was obtained irrespective of kinds of manganese promoter.

Influence of oxygen pressure upon oxidation of cyclohexane is shown in Table 3. As the oxygen pressure increased, the conversion of cyclohexane increased linearly. This suggests that dissolution of oxygen is the rate-determining step or that oxygen is directly contributing to important reaction steps. When the amount of isoamyl nitrite was varied, the conversion increased proportionally (vide supra). Therefore, at least oxygen pressure of 0.91 MPa is circumventing the oxygen dissolution limitation. As expected, at low oxygen pressure the selectivity for cyclohexanol was high and at higher oxygen pressure the selectivity for AA increased.

The novel catalyst system was applied to other cycloalkanes, namely cyclopentane and cyclooctane (Table 4). For both cycloalkanes, formation of dicarboxylic acids was observed.

Fig. 4. Arrhenius plot for oxidation of cyclohexane. Cyclohexane 64 mmol, isoamyl nitrite 5 mol%, Co(acac)$_3$ 0.04 mol%, Mn(acac)$_3$ 0.04 mol%, P_{O_2} 0.91 MPa and 3 h.

Table 2
Influence of amount of isoamyl nitrite and kinds of manganese promoters upon product distribution

Run no.	Isoamyl nitrite (mol%)	Co(acac)$_3$ (mol%)	Mn(acac)$_3$ (mol%)[a]	Conversion (%)	Selectivity (%)		
					Cyclohexanol	Cyclohexanone	Adipic acid
1	5.0	–	–	6.7	58.4	18.9	22.7
5	5.0	0.04	0.04	9.7	52.7	11.9	35.4
6	1.0	0.04	0.04	5.2	51.6	19.1	29.4
7	2.5	0.04	0.04	7.7	47.0	15.2	37.8
8	10.0	0.04	0.04	6.7	67.6	12.2	20.2
9	5.0	0.04	0.20[b]	8.0	53.8	7.2	39.0
10	5.0	0.04	0.18[c]	9.2	50.2	10.4	39.4
11	5.0	0.04	0.17[d]	8.8	54.5	6.4	39.2

Cyclohexane 64 mmol, 120 °C, P_{O_2} 0.91 MPa and 3 h.
[a] mol% as Mn.
[b] MnO.
[c] Mn$_2$O$_3$.
[d] MnO$_2$.

Table 3
Influence of oxygen pressure upon oxidation of cyclohexane

Run no.	Oxygen pressure (MPa)	Conversion (%)	Selectivity (%)		
			Cyclohexanol	Cyclohexanone	Adipic acid
12	0.10[a]	0.0	0.0	0.0	0.0
13	0.31	4.1	74.1	2.5	23.4
14	0.61	7.9	54.2	15.4	30.4
5	0.91	9.7	52.7	11.9	35.4

Cyclohexane 64 mmol, isoamyl nitrite 5 mol%, Co(acac)$_3$ 0.04 mol%, Mn(acac)$_3$ 0.04 mol%, 120 °C and 3 h.
[a] Air oxidation.

Table 4
Oxidation of cyclopentane and cyclooctane

Run no.	Substrate	Conversion (%)	Selectivity (%)		
			Alcohol	Ketone	Dicarboxylic acid
15[a]	Cyclopentane	2.3	18.5	27.2	54.3
5[b]	Cyclohexane	9.7	52.7	11.9	35.4
16[c]	Cyclooctane	15.1	52.2	35.2	12.6

Cycloalkane 64 mmol, isoamyl nitrite 5 mol%, Co(acac)$_3$ 0.04 mol%, Mn(acac)$_3$ 0.04 mol%, 120 °C and 3 h.
[a] P_{O_2} 0.63 MPa.
[b] P_{O_2} 0.91 MPa.
[c] P_{O_2} 1.04 MPa.

Fig. 6. Time courses of conversion of cyclohexane and decomposition of isoamyl nitrite. Cyclohexane 64 mmol, isoamyl nitrite 5 mol%, 120 °C and P_{O_2} 0.91 MPa.

Especially, in the case of cyclopentane very high glutaric acid selectivity exceeding 50% was obtained, though cyclopentane conversion was one fourth of the cyclohexane conversion. In contrast, the conversion of cyclooctane was higher than that of cyclohexane. However, suberic acid selectivity was about one third of adipic acid selectivity. These results indicate that our novel catalyst system is useful for the direct formation of dicarboxylic acids from the corresponding cyclic alkanes.

Hereafter, we would like to discuss the reaction mechanism in detail. Firstly, influence of the reaction temperature upon decomposition of isoamyl nitrite was studied (Fig. 5). At 80 °C, the decomposition was not completed in 6 h. At 100 °C, the decomposition reached 100% after 6 h. At 120 °C, the decomposition rate was very fast and in less than 60 min the decomposition was completed.
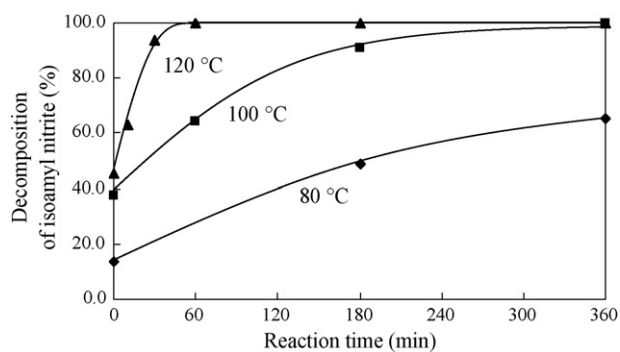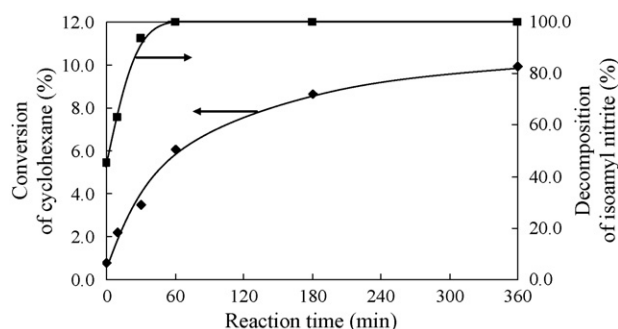
Fig. 6 shows time courses of conversion of cyclohexane and decomposition of isoamyl nitrite without any promoters. When the reaction time was 0 min, already half of isoamyl nitrite was decomposed. This is because the decomposition occurred during temperature rise to 120 °C. During this period, the conversion of cyclohexane was very low, less than 1%. Decomposition of the nitrite was completed in 1 h, however, the conversion of cyclohexane increased continuously up to 6 h. Here, we should consider at least following two possibilities: one possibility is that NO formed by decomposition of nitrite reacted with cyclohexanol or isoamyl alcohol to reproduce nitrite and the other is that radical chain reaction continued. If the former is correct, the turn-over number reaches almost two and the reaction can be said catalytic. If the latter is working, the nitrite should be considered as a reaction initiator and the reaction is not catalytic.
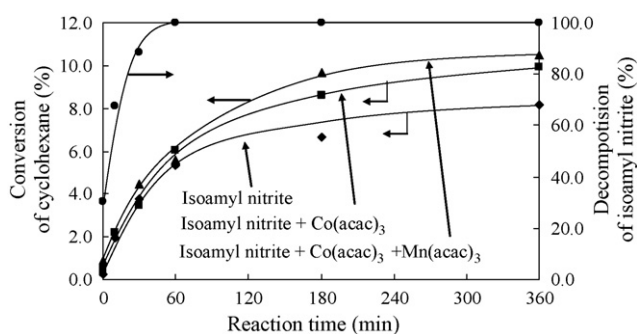

Fig. 5. Influence of reaction temperature upon decomposition of isoamyl nitrite. Cyclohexane 64 mmol, isoamyl nitrite 5 mol%, Co(acac)$_3$ 0.04 mol% and P_{O_2} 0.91 MPa.

Fig. 7. Influence of addition of promoter upon conversion of cyclohexane. Cyclohexane 64 mmol, isoamyl nitrite 5 mol%, Co(acac)$_3$ 0.04 mol%, Mn(acac)$_3$ 0.04 mol%, 120 °C and P_{O_2} 0.91 MPa.

Table 5
Comparison of isoamyl nitrite and cyclohexane–NO systems on oxidation of cyclohexane

Run no.	Isoamyl nitrite (mmol)	Cyclohexanol (mmol)	NO (mmol)	Conversion (%)	Selectivity (%)		
					Cyclohexanol	Cyclohexanone	Adipic acid
1[a]	3.2	–	–	6.7	58.4	18.9	22.7
17[b]	–	3.2	3.2	2.0	49.5	22.9	27.5

Cyclohexane 64 mmol, 120 °C and 3 h.
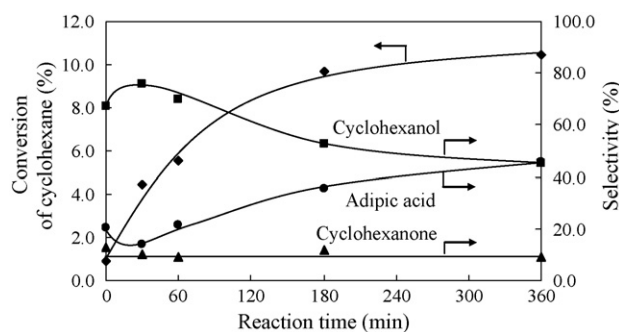[a] P_{O_2} 0.91 MPa.
[b] P_{O_2} 0.75 MPa.

Fig. 8. Time course of cyclohexane oxidation on the ternary system of nitrite, Co and Mn. Cyclohexane 64 mmol, isoamyl nitrite 5 mol%, Co(acac)$_3$ 0.04 mol%, Mn(acac)$_3$ 0.04 mol%, 120 °C and P_{O_2} 0.91 MPa.

Fig. 7 shows the relation between the decomposition of the nitrite and the conversion of cyclohexane with various catalyst systems. To the time when the decomposition of the nitrite was completed, conversion curves were quite similar among the catalyst systems. Only after 1 h, the differences appeared. The order of the conversion of cyclohexane was as follows; nitrite + Co + Mn > nitrite + Co > nitrite. This suggests that the reaction was promoted mainly by the nitrite up to 1 h and that thereafter promoters contributed mainly.

The selectivity change during the course for the system consisting of the nitrite, Co(acac)$_3$ and Mn(acac)$_3$ is shown in Fig. 8. Up to 1 h, the selectivity for cyclohexanol was very high and thereafter decreased with concomitant increase in adipic acid selectivity. Therefore, adipic acid is produced at the latter reaction stage where promoters, especially Mn(acac)$_3$, are working.

The possibility of in situ nitrite formation from cyclohexanol and NO was investigated (Table 5). Here, equimolar amount of cyclohexanol to isoamyl nitrite was used together with NO. Selectivities of products were nearly the same. However, compared to the result with isoamyl nitrite, the cyclohexanol and NO system gave lower cyclohexane conversion. This suggests that cyclohexyl nitrite could be formed in situ even in the presence of oxygen but that the rate of cyclohexyl nitrite formation is rather slow. Actually, the formation of cyclohexyl nitrite was confirmed from the solution after the oxidation by gas chromatography.

To study in situ formation of nitrite in more detail, NO was added to the typical reaction system (Table 6). As oxygen pressure was arranged when the temperature reached 120 °C, the actual partial pressure of oxygen was 0.78 MPa. As shown in Table 6, selectivities of products remained almost unchanged and only the conversion fell to about 75% of that without NO addition. As Table 3 shows, the conversion is linearly proportional to the oxygen pressure. Then, this decrease in the conversion is rationally explained by the dependence on the oxygen pressure. Therefore, contribution of reproduction of nitrite during the reaction is minimal, and this concludes that nitrite is not a catalyst but the reaction proceeds by the radical chain reaction mechanism.

Table 7 shows the results on oxidation of intermediates, cyclohexanol and cyclohexanone, with various catalyst systems. The system consisting of the nitrite, Co(acac)$_3$ and Mn(acac)$_3$ gave high conversions for both raw materials in 30 min. This means that the rate-determining step for direct adipic acid formation is not the oxidation of either cyclohexanol or cyclohexanone, but the oxidation of cyclohexane. It should be noted that Mn(acac)$_3$ had very low activity for cyclohexanol oxidation, which is in clear contrast to the fact that Mn(acac)$_3$ catalyzed cyclohexanone oxidation effectively.

Over-all reaction scheme is shown in Fig. 9. Firstly, isoamyl nitrite decomposes to isopentyl oxy radical and NO radical just by heating. Cyclohexyl radical is formed by subtraction of hydrogen of cyclohexane with the isopentyl oxy radical. The cyclohexyl radical then reacts with oxygen to form cyclohexane peroxy radical and this radical subtracts hydrogen from another cyclohexane to reproduce the cyclohexyl radi-

Table 6
Influence of addition of NO upon oxidation of cyclohexane

Run no.	NO (mmol)	Conversion (%)	Selectivity (%)		
			Cyclohexanol	Cyclohexanone	Adipic acid
5[a]	–	9.7	52.7	11.9	35.4
18[b]	2.7	7.2	57.3	8.3	34.4

Cyclohexane 64 mmol, isoamyl nitrite 5 mol%, Co(acac)$_3$ 0.04 mol%, Mn(acac)$_3$ 0.04 mol%, 120 °C and 3 h. NO was added before the reaction.
[a] P_{O_2} 0.91 MPa.
[b] P_{O_2} 0.78 MPa.

Table 7
Oxidation of cyclohexanol and cyclohexanone

Run no.	Raw material	Isoamyl nitrite (mol%)	Co(acac)$_3$ (mol%)	Mn(acac)$_3$ (mol%)	Conversion (%)	Selectivity (%)	
						Cyclohexanone	Adipic acid
19	Cyclohexanol[a]	5	–	–	6.6	67.4	32.6
20		–	0.04	–	6.8	89.7	10.3
21		–	–	0.04	0.3	100.0	0.0
22		5	0.04	–	7.0	61.3	38.7
23		5	0.04	0.04	8.8	78.2	21.8
24	Cyclohexanone[b]	5	–	–	3.0	–	100.0
25		–	0.04	–	4.0	–	100.0
26		–	–	0.04	4.5	–	100.0
27		5	0.04	–	5.1	–	100.0
28		5	0.04	0.04	10.4	–	100.0

Cyclohexanol or cyclohexanone 64 mmol, 120 °C, 30 min.
[a] P_{O_2} 1.06 MPa
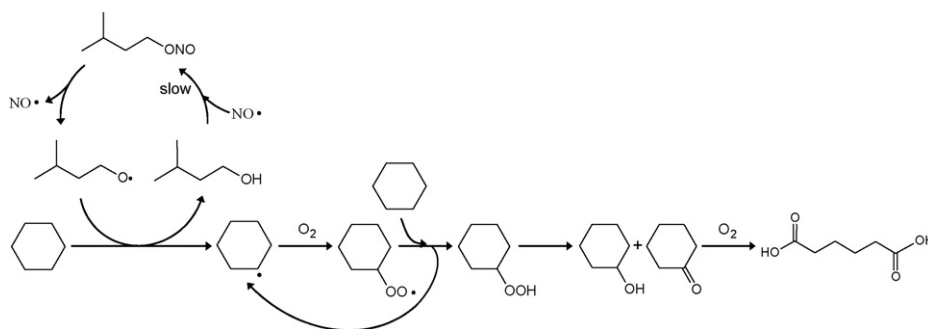[b] P_{O_2} 1.04 MPa.

Fig. 9. Estimated reaction scheme.

cal and to form the cyclohexane hydroperoxide. Thereafter, the hydroperoxide decomposes to cyclohexanol and cyclohexanol is consecutively oxidized to adipic acid through cyclohexanone. The rate-determining step is the initial formation of cyclohexyl radical and the nitrite contributes mainly to this step. Oxidation of cyclohexanol and cyclohexanone was rather fast and Co(acac)$_3$ and Mn(acac)$_3$ catalyzed mainly these steps. The step to reproduce nitrites is possible but slow. This may be because NO is easily consumed to NO$_2$ [25,26].

4. Conclusions

Adipic acid was directly obtained by oxidation of cyclohexane using novel system composed of isoamyl nitrite, Co(acac)$_3$ and Mn(acac)$_3$. Mainly, the nitrite contributed to the rate-determining step, the initial dissociation of C–H bond of cyclohexane, and Co and Mn promoters contributed to the consecutive oxidation steps. The best reaction conditions were 5 mol% isoamyl nitrite, 0.04 mol% Co(acac)$_3$, 0.04 mol% Mn(acac)$_3$ at 120 °C and P_{O_2} 0.91 MPa, and the high adipic acid selectivity of about 40% was attained.

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