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Oxidation of cyclohexene by dendritic PAMAMSA-Mn(II) complexes

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Abstract

Six dendritic PAMAMSA-Mn (II) complexes were synthesized and were well characterized. The oxidation of cyclohexene under 1 atmospheric pressure of molecular oxygen in the absence of any solvent with the synthesized complexes was employed to value their catalytic properties. It was shown that all the dendritic complexes with different generation numbers (*G*) exhibit promising catalytic activities for the oxidation. Under the mild condition, all the oxidations give 7-oxabicyclo[4,1,0]heptane **1**, 2-cyclohexen-2-ol **2**, 2-cyclohexen-2-one **3** and 7-oxabicyclo [4,1,0]heptan-2-one **4** as the major products. The factors that affect the oxidations were also well investigated under identical conditions.

Keywords: Dendrimer; Complexes; Catalysis; Oxidation; Cyclohexene

1. Introduction

Since the pioneering divergent synthesis of dendrimers by Tomalia et al. [1] and Newkome et al. [2] and the convergent synthesis methodology by Hawker and Frechet [3], many different types of dendritic macromolecules have been prepared [4–7]. With about two decades' development, much attention is now emphasized on the functional dendrimers [8,9]. On the other hand, because of their unique properties, dendritic catalysts have been a major part of the metallodendrimers, and many of research have been documented [10–12].

Metal-containing compound are the chiefly used catalysts for all kinds of oxidation possesses, such as Cu- and Co-containing complexes, etc. [13–15]. Among all of these catalysts, Mn-containing compounds of Schiff-base supported complexes are reported to give best results with hydrogen peroxide, organic hydroperoxides, molecular oxygen, as well as other single-oxygen atom transfer reagents [16–19]. Salvadori and co-workers have carried out much of achievement on varies of reactions by polymer- supported salen-complexes as catalysts [20,21].

The advantages of the metallodendritic catalysts consists in their unique properties results from their esthetic molecular structures. The extremely asymmetric molecular framework enhances their catalytic selectivity in some reactions. The highly peripheral functionalities ensure their highly catalytic activities through the transformational process. At the same time, their special backbones can result in the heterogeneous reaction conditions. This could make for the reusing of the catalysts as well as the lightening of environmental pollution. The study of metallodendritic catalysts may give lights on green chemistry.

Because of the high catalytic reactivity and the wide using of the Mn-containing complexes, it is the first choice of our research. Another reason is we wondered to know how about their catalytic performance in the molecular-oxygen-oxidation instead of the usually used hydrogen peroxide, organic hydroperoxides oxidant. Enhance we report herein a new type of PAMAMSA-Mn(II) metallodendrimers derives from the well-known polyamidoamine (PAMAM) dendrimers. The properties of the synthesized complexes were well characterized. When concerning their catalytic activities for the oxidation of cyclohexene under mild condition, all the catalysts show promising activities for the reactions as expected.

2. Experimental

2.1. Reagents

Methyl acrylate (MA), AR, ethylenediamine (EDA), AR, cyclohexene, CP, salicyaldehyde (SA), CP, were all

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obtained from commercial source and purified before using. $Mn(OAc)_2{\cdot}4H_2O$, AR, was also from commercial source. All of other solvents are analytical reagents.

2.2. Synthesis

2.2.1. Synthesis of polyamidoamine (PAMAM) dendrimers with different generation numbers

The PAMAM dendrimers with different generation numbers were synthesized according to the literature [1,22]. Methyl acrylate (MA) and ethylenediamine (EDA) were used as substrates. The synthesis of the PAMAM dendrimers involves the following processes: (a) the Michael-addition of amine groups in EDA to MA under 50 °C in methanol solution (affords the dendritic product of 0.5 generation (*G*) with ester groups terminated) and (b) the amidation of the terminal ester groups of 0.5*G* dendrimer from dissolving in methanol solution by excessive EDA under 50 °C (affords the 1.0*G* dendrimer with terminal amine groups) and (c) distillation of exceeded EDA under reduced pressure (gives the purified 1.0*G* dendrimer). Then the circled Michael-additions of MA by the terminal amine groups in the integral-numbered dendrimers and the amidations of peripheral ester groups in half integral-numbered dendrimers by excessive EDA give the PAMAM dendrimers with different generation numbers. All the synthesized dendrimers with different generation numbers are shown as yellow ropy liquid.[1] The dendrimers with integral generation numbers ($G = 1, 2, 3, 4, 5, 6$) were then put into the synthesis of the dendritic PAMAMSA ligands.

2.2.2. Synthesis of dendritic PAMAMSA ligands

The condensation reactions between the PAMAM dendrimers with integral *G* and SA were employed to synthesize the PAMAMSA ligands. The PAMAM dendrimers were dissolved in methanol solution with stirring by a magnetic stirring bar until they were well dissolved. Then the stoichiometric SA was added to the solution. It can be found that much of yellow precipitation was appeared. Stirring the suspension for 2 h at 50 °C, then cooled the suspension, and the yellow products was found. The suspension was filtrated and the deposition was washed with cooled ethanol. The deposition was dried in vacuum below 40 °C, then the yellow powder, PAMAMSA dendritic ligands with different *G* were obtained.

2.2.3. Synthesis of dendritic PAMAMSA-Mn(II) complexes

The synthesized PAMAMSA ligands with different *G* were dissolved in heated ethanol. Concerning for the possible completely coordination, we added two times amount of stoichiometric $Mn(OAc)_2{\cdot}4H_2O$ to the yellow solutions, stirred and refluxed for 2 h, then cooled the solution, yielded the brown solutions and some depositions. The suspensions were then filtrated and the precipitations were washed with cool methanol and petroleum ether in turn, then the brown dendritic PAMAMSA-Mn(II) catalysts were obtained. The products were then in vacuum dried under 60 °C for a night. The structure of the dendritic PAMAMSA-Mn(II) complexes ($G = 3.0$) are shown below (Fig. 1).

[1] If methyl acrylate was not post purified under reduced-pressure under 40 °C beforehand, all the yielded dendritic products appearances as red ropy liquid.

3. Results and discussion

3.1. Characterization of the synthesized products

3.1.1. The IR spectra data of the ligands and the complexes

The IR spectra of the synthesized the dendritic ligands and the resulting complexes were obtained by using a Nicolet AVATAR 360 FT-IR spectrophotometer. The resulting FT-IR data of the ligands and the complexes were shown in the Tables (Tables 1 and 2) and the Figures (Figs. 2 and 3).

From the Tables and the Figures we can find that all the absorption signal of the functional groups existing within the ligands appear in the spectroscopy. It confirmed that the dendritic structures have been formed. Table 3 showed that the characteristic absorption of M-N and M-O was also found. This indicates that all the ligands and the complexes we expected have been well prepared.

3.1.2. Data of the PAMAMSA-Mn(II) complexes

ICP content of the PAMAMSA-Mn(II) complexes were analyzed on a Shimadzu ICPV-1000S and an American ICPV-5600 analytic instruments. All the analyses were carried out on standard conditions. The contents of manganese in the six synthesized complexes were shown in Table 3.

It can be seen from the Table that the ICP data of the six synthesized complexes deviate from the calculated results according to the metal ions only coordinated with the peripheral schiff-base groups. This means that the structures of the complexes are partially irregular comparing to their idealized frameworks. From the ideal structures of the ligands we know that the Mn(II) ions not only can coordinated with the peripheral schiff-base groups, but also can coordinated with the inner nitrogen atoms existing all over within the ligand molecular backbone. On the other hand, due to the unique “exterior thickness and inner thinness” molecular model, the big cavity in the ligands’ structures can also trap many of the Mn(II) ions in their molecular cores. Another reason is that the high density of the coordination positions will lead to some coordinating “defects” in the complexes, and the “defects” results from the synthesis of the dendrimers will also bring some irregularities from the initiation. Due to the reasons above, the examined ICP data give much difference from those of the ideally calculated ones.

3.1.3. The theoretical molecular weight of the ligands and the complexes

Due to the special molecular structures and the unique properties of the dendrimers, their molecular weight is

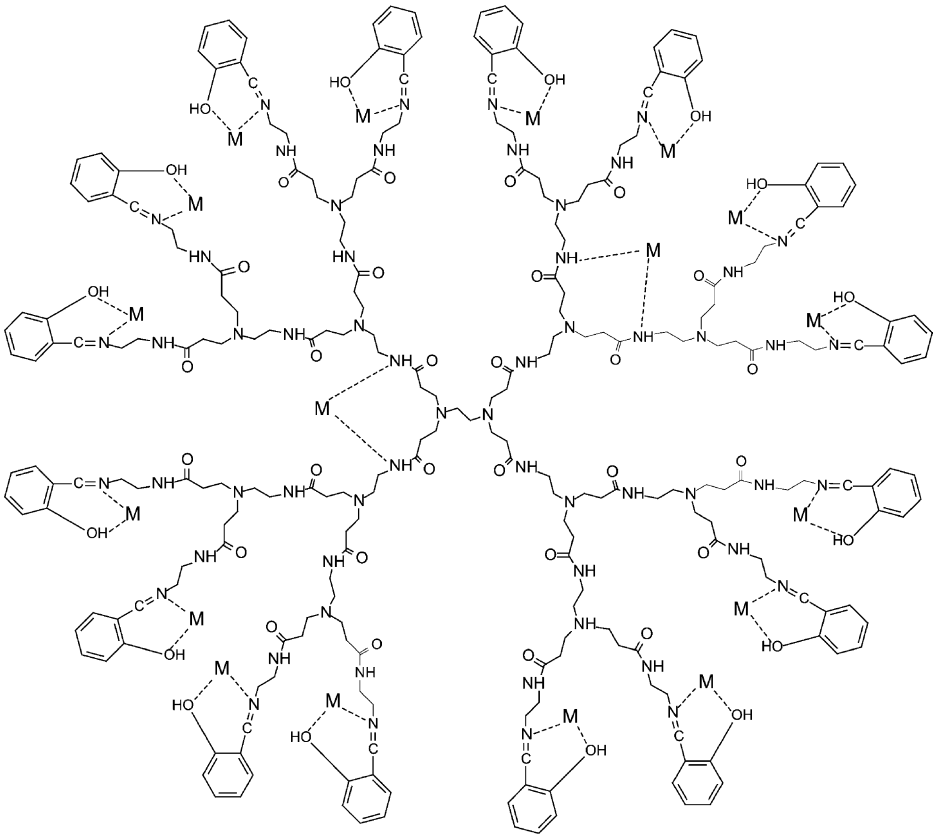


Fig. 1. The structure of the synthesized dendritic PAMAMSA-Mn(II) complexes ($G = 3.0$). The peripheral amino groups were functionalized by salicyaldehyde in order to form schiff-base type ligands.

Table 1
The FT-IR data of the PAMAMSA ligands (cm^{-1})

PAMAMSA (*n*.0)	ν_{CONH}	$\nu_{=C-H}$	ν_{ϕ}	δ_{ϕ}	$\delta_{CH-\phi}$	$\nu_{>N-}$	$\nu_{CH-\phi}$
PAMAMSA (1.0)	3051.58	3004.64	1575.93	746.38	1206.85	1147.68	854.86
PAMAMSA (2.0)	3051.86	3005.47	1576.05	746.65	1207.53	1148.20	854.78
PAMAMSA (3.0)	3051.47	3004.82	1575.99	746.37	1207.24	1147.89	854.62
PAMAMSA (4.0)	3051.42	3005.39	1577.53	747.58	1210.07	1148.78	854.81
PAMAMSA (5.0)	3051.27	3004.70	1576.01	746.46	1207.16	1148.09	854.96
PAMAMSA (6.0)	3051.40	3004.72	1576.28	746.75	1207.31	1148.25	855.25

not in keeping with the equation: $[\eta] = KM^a$. It means that we could not calculate their molecular weight through examining their viscosity. Furthermore, there is no suitable K for the equation. But their regular three dimensional molecular structures and the asymmetric molecular skeleton confirmed that the theoretical molecular weight can be calculated according to their formula. The theoretically calculated molecular weight of the synthesized ligands and the complexes were shown in Table 4.

Table 2
The FT-IR data of the PAMAMSA-Mn(II) complexes (cm^{-1})

PAMAMSA (*n*.0)-Mn	$\nu_{(M-N)}$	$\nu_{(M-O)}$
PAMAMSA (1.0)-Mn	623.80	453.08
PAMAMSA (2.0)-Mn	624.32	453.67
PAMAMSA (3.0)-Mn	623.47	452.94
PAMAMSA (4.0)-Mn	624.20	453.99
PAMAMSA (5.0)-Mn	622.50	453.10
PAMAMSA (6.0)-Mn	622.89	453.37

Table 3
The Mn content of the six complexes by ICP determinations

Complexes (generation numbers in parentheses)	ICP data (%)
PAMAMSA (1.0)-Mn(II)	21.35
PAMAMSA (2.0)-Mn(II)	20.53
PAMAMSA (3.0)-Mn(II)	19.58
PAMAMSA (4.0)-Mn(II)	15.31
PAMAMSA (5.0)-Mn(II)	25.69
PAMAMSA (6.0)-Mn(II)	22.35

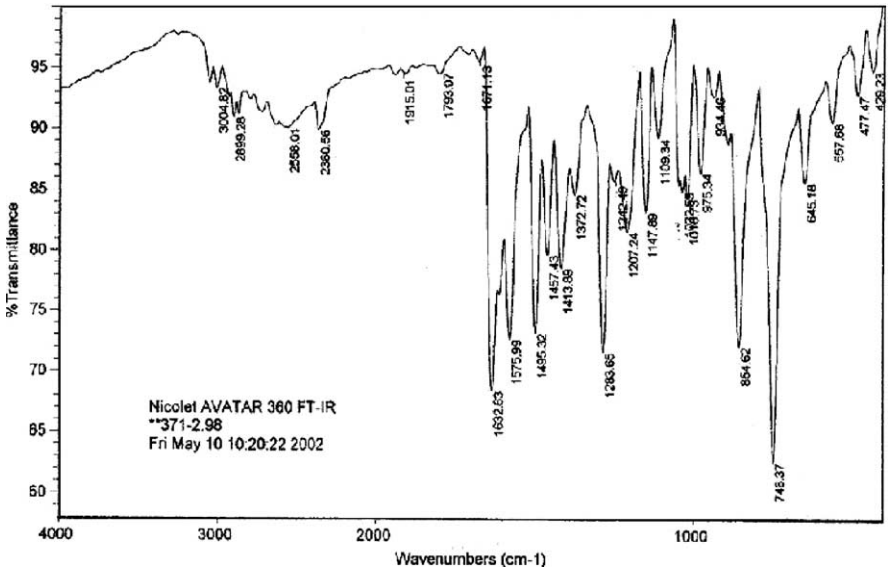


Fig. 2. IR spectra of PAMAMSA (3.0) ligand by a Nicolet AVATAR 360 FT-IR spectrophotometer.

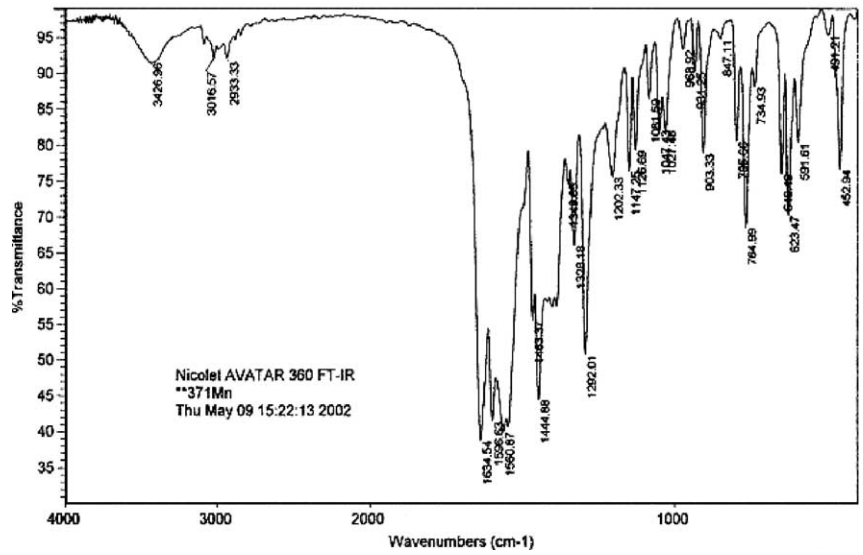


Fig. 3. IR spectra of PAMAMSA (3.0)-Mn(II) complex by a Nicolet AVATAR 360 FT-IR spectrophotometer.

Table 4
The theoretical molecular weight of the ligands and the complexes (g/mol)

PAMAMSA (*n*.0)	Calculated molecular weight	PAMAMSA (*n*.0)-Mn(II)	Calculated molecular weight
PAMAMSA (1.0)	932	PAMAMSA (1.0)-Mn	1152
PAMAMSA (2.0)	2260	PAMAMSA (2.0)-Mn	2700
PAMAMSA (3.0)	4916	PAMAMSA (3.0)-Mn	5796
PAMAMSA (4.0)	10228	PAMAMSA (4.0)-Mn	11988
PAMAMSA (5.0)	20852	PAMAMSA (5.0)-Mn	24372
PAMAMSA (6.0)	42100	PAMAMSA (6.0)-Mn	49140

3.2. Catalytic properties studies

In order to detect the catalytic properties of the resulting PAMAMSA-Mn(II) complexes, the complexes were used to the catalytic oxidation of cyclohexene with molecular oxygen under 1 atmospheric pressure in the absence of solvents. The results show that all the six complexes with different generation numbers exhibit promising catalytic activities for the oxidation. In this condition, the oxidation of cyclohexene gives 7-oxabicyclo[4,1,0]heptane **1**, 2-cyclohexen-2-ol **2**, 2-cyclohexen- 2-one **3** and 7-oxabicyclo[4,1,0]heptan-2-one **4** as the major products. The oxidation patterns are shown below (Fig. 4).

The product **4** is the first reported synthesized product through this kind of oxidation process, and this will give

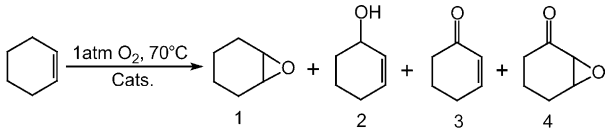


Fig. 4. The major product of the oxidation of cyclohexene by PAMAMSA (1–6*G*)-Mn(II) catalysts with molecular oxygen as oxidant.

some convenience for some organic synthesis as well as for the synthesis of some of the pharmaceutical intermediates.

All the factors, including temperature, time, ratio of catalysts/substrate, solvents as well as additives were investigated in the following.

3.2.1. The catalytic properties of the six complexes

All the complexes perform promising catalytic activities in the oxidation of cyclohexene under normal condition. The oxidations were carried out in a 25 ml branched flask stirred by a magnetic bar. All the product of the oxidation were determined on a GC (instrument: Shimadzu GC-16A spectrophotometer, with a OV-17 filled pillar of 3 m × 3 mm, determined by a FID inspecting instrument with a temperature range of 80–220 °C. The increased procedure of the temperature is 15 °C/s) and a GC/MS spectrophotometer (instrument: QP-1000A GC/MS system, a capillary pillar was used. Other conditions are same as GC system). The concentration of the each product was automatically analyzed by the spectrophotometer. The results of the oxidation were shown in Table 5.

It can be seen from the Table that all the complexes with different generation show catalytic activities for the oxidation of cyclohexene under mild condition. The value of oxygen consumption shows a curve-like change with the variation of the catalysts' generation. Table 5 also showed that the selectivity of product **1** is always the lowest, while the selectivity to product **4** is the highest. There is no great change within the selectivity of products **2** and **3**. We can conclude from the Table that because the product **4** is the major product, this catalytic system will give us promising results for its highest selectivity for the formation of the unique product 7-oxabicyclo[4,1,0] heptan-2-one 4.

3.2.2. The effect of relevant factors on the oxidation

All of the relevant factors of the oxidation were well investigated. Because of the relatively higher catalytic property of the third generation complex among all of the six synthesized complexes, the PAMAMSA (3.0)-Mn catalysts was used as a model catalyst for the investigation of these factors.

3.2.2.1. The temperature. The temperature of the oxidation system was controlled by a temperature controller instrument. In order to investigate the effect of temperature on the oxidation, we carried out the reaction under different temperature, such as 80, 70, 60, 50 and 40 °C. It showed that the reaction temperature gives great influence on the oxidation. Too high or too low temperature is unfavorable for the results of the reactions. The results are concluded in Table 6.

It is shown in the Table that at 40 °C, the reactivity of the catalysts reaches to its lowest; This trend can be reflected by the degreasing of the value of oxygen consumption. On the other hand, it was seen that at lower temperature, the oxidation give higher selectivity of product **4** compared to that at the higher temperature, this result suggest that

Table 5
The catalytic properties of the PAMAMSA-Mn(II) complexes[a]

Complexes	Oxygen consumption (ml/molar catalyst)	Products selectivity (%)			
		1	2	3	4
PAMAMSA (1.0)-Mn	1.11×10^7	5	22	30	42
PAMAMSA (2.0)-Mn	0.88×10^7	6	18	26	50
PAMAMSA (3.0)-Mn	0.90×10^7	5	24	39	32
PAMAMSA (4.0)-Mn	1.93×10^7	6	25	36	32
PAMAMSA (5.0)-Mn	1.92×10^7	7	21	25	46
PAMAMSA (6.0)-Mn	2.05×10^7	10	23	31	36

[a] Condition: cyclohexene: 5 ml, PAMAMSA (3.0)-Mn: 2 mg, 1 atm O_2, 6 h at 70 °C.

Table 6
The effect of temperature on the oxidation by the PAMAMSA (3.0)-Mn catalysts[a]

Temperature (°C)	Oxygen consumption (ml/molar catalyst)	Products selectivity (%)			
		1	2	3	4
80	2.42×10^7	5	26	41	28
70	0.98×10^7	6	24	39	32
60	0.90×10^7	5	18	27	49
50	0.51×10^7	6	17	28	49
40	0.50×10^7	7	16	31	46

[a] Condition: cyclohexene: 5 ml, PAMAMSA (3.0)-Mn: 2 mg, 1 atm O_2 and 6 h.

Table 7
The influence of reaction time on the oxidation by the PAMAMSA (3.0)-Mn catalysts[a]

Time (h)	Product selectivity (%)			
	1	2	3	4
1	3	32	36	29
2	2	25	31	42
3	2	24	30	44
4	2	23	30	45
5	6	17	27	50

[a] Condition: cyclohexene 5 ml, PAMAMSA (3.0)-Mn: 2 mg, 1 atm O_2, 70 °C.

the product **4** is not stable in high temperature. We also tuned the reaction temperature more than 80 °C or higher, only to find that the substrate of cyclohexene evaporated quickly. At the same time, due to the vaporized cyclohexene atmosphere which spreading above the substrate, the oxidant of O_2 was separated from the contacting of cyclohexene. Under this condition, the oxidation could not be carried out at all. From the former investigation, it is suggested that the optimum temperature of the oxidation is 70 °C.

3.2.2.2. The reaction time. The effect of reaction time on the oxidation as well as on the selectivity to the four products was also detailed in this system by a time controller. We took out of 0.01 ml reaction mixture from the branch of the reaction flask during a same interval by a syringe. Then the reaction mixture was immediately analyzed with GC. The results were listed in Table 7.

The results show that longer reaction time gives higher selectivity to the product **4**, at the same time, the selectivity to **1**(5 h) is also increased. Under identical condition, the oxidation conversion after 8 h is not changed obviously with the prolonging of the reaction time (from 5 to 8 h).

3.2.2.3. The ratio of catalysts to substrate. Different ratios of catalyst to substrate were employed to investigate the corresponding variation of the oxidation result. We stabilized the value of the substrate, and changed the milligram of the catalyst. The oxidation results were changed along with the variation of the amount of the catalyst used. The oxidation results using different catalyst to substrate ratios are shown in Table 8.

It can be concluded from Table 8 that with the increasing of the ratio of catalysts to substrates, the value of oxygen consumption become lower and lower. At the same time, the ratio of 1 mg/5 ml gives the highest selectivity of product **4** under the identical condition. It means that the higher ratio would not suitable for the formation of product **4**.

3.2.2.4. The solvent. In the investigation of catalytic activity of the synthesized complexes, we wondered how about the other factors, such as different solvents as well as the additives, acted on the oxidations. With this aim, the oxidations were carried out with different solvents. The effect of solvents is shown in Table 9.

It can be seen from Table 9 that among the five kinds of solvent, DMSO gives the highest selectivity of the yield. In this condition, only 7-oxabicyclo [4.1.0]heptane is found as the only product. But the conversion of the substrate is the lowest. As the typical of nonpolar solvents, dioxane and cyclohexane give the higher selectivity of product **4**, while as the polar ones, however, ethanol and nitrobenzene give the higher selectivity of product **3**, and there is no product of **4**. From all above we can conclude that a nonpolar solvent would give higher selectivity of the product **4**, while

Table 8
The influence of different ratio on the oxidation by the PAMAMSA (3.0)-Mn catalysts[a]

Ratio (mg/ml)	Oxygen consumption (ml/molar catalyst)	Product selectivity (%)			
		1	2	3	4
0.5/5	12.04×10^7	6	25	30	38
1/5	1.20×10^7	6	19	26	54
2/5	0.90×10^7	6	24	30	45

[a] Condition: cyclohexene 5 ml, 1 atm O_2, 6 h at 70 °C.

Table 9
The influence of solvent on the oxidation by the PAMAMSA (3.0)-Mn catalysts[a]

Solvent	Oxygen consumption (ml/molar catalyst)	Conversion (%)	Product of selectivity (%)			
			1	2	3	4
DMSO	1.07×10^7	13	100	/	/	/
Dioxane	2.51×10^7	37	5	13	31	52
Cyclohexane	2.31×10^7	31	10	13	26	51
Ethanol	1.40×10^7	45	8	19	71	2
Nitrobenzene	1.54×10^7	34	10	26	2	1

[a] Condition: cyclohexene 2.0 ml, PAMAMSA (3.0)-Mn: 0.8 mg, solvent 2.0 ml, 1 atm O_2, 6 h at 70 °C.

Table 10
The influence of different volume of acetic acid on the oxidation by the PAMAMSA (3.0)-Mn catalysts[a]

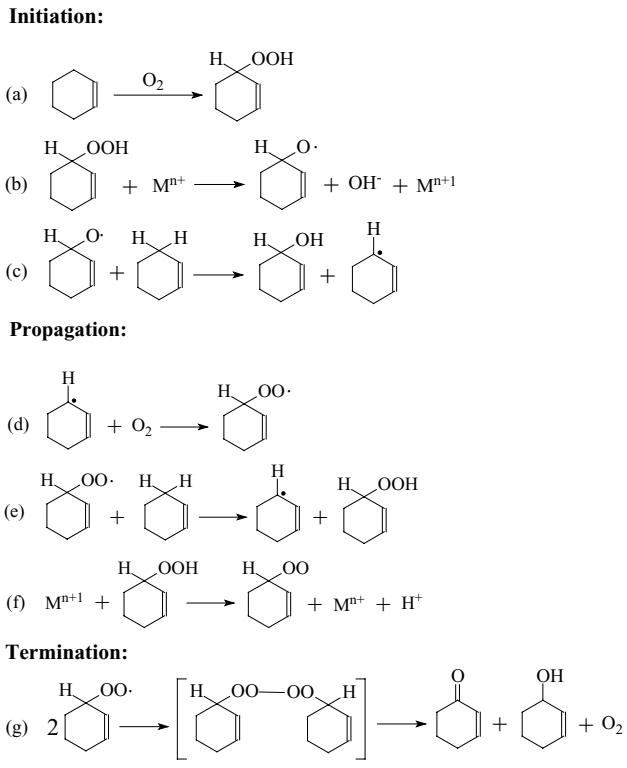
Volume (ml)	Product selectivity (%)			
	1	2	3	4
0.25	1	31	49	18
0.50	3	34	42	22
0.75	0.5	28	44	27
1.00	1	30	39	30

[a] Condition: cyclohexene 2 ml, PAMAMSA (3.0)-Mn: 0.8 mg, 1 atm O_2, 6 h at 70 °C.

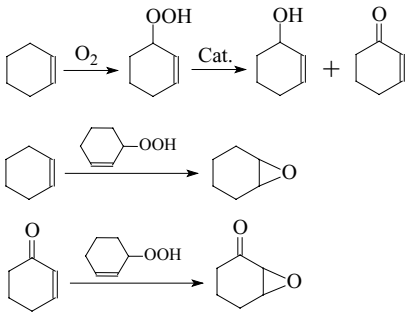
a polar solvent give higher selectivity of product **3** in this oxidation.

3.2.2.5. The additives. In this condition, acetic acid and pyridine were chosen as the typical additives of acid and base, respectively. It was shown from the reaction that acetic acid would accelerate the completing of oxidation, while pyridine terminates the reaction. The effect of different value of acetic acid on the oxidation was well investigated, too. The results are shown in Table 10.

It is shown in the Table that with the increasing of the volume of acetic acid, the oxidation would give **3** as the major product. When concerning to the selectivity of product of **2**, **3**, and **4**, we can find that the increasing of the volume would only to tune the roughly equal of the selectivity of the three. This suggests that much more amount of acidic additives would not useful for the selectivity of the oxidation.



Scheme 1. The classic Haber–Weiss radical-chain sequence mechanism proposed for the oxidation of cyclohexene by the PAMAMSA-Mn(II) complexes based on the research of Weiner, etc. [23–27].



Scheme 2. The obtaining of the four major products by the oxidation according to the proposed mechanism.

4. Mechanism

In order to explain how the oxidation was occurred, and how the four major products were formed, from the literatures [23–27,16] and the analysis of the relevant factors of the oxidation, a classic Haber–Weiss radical-chain sequence mechanism was proposed (Scheme 1).

Oxidation of cyclohexene and 2-cyclohexen-2-one by 2-cyclohexen-hydroperoxide give 7-oxabicyclo[4,1,0]heptane and 7-oxabicyclo[4,1,0]heptan-2-one, respectively (Scheme 2) [28].

5. Conclusions

The dendritic PAMAMSA-Mn(II) complexes show promising catalytic activities for the oxidation of cyclohexene under 1 atm molecular oxygen. The major product of the oxidation are 7-oxabicyclo[4.1.0]heptane, 2-cyclohexen-2-ol, 2-cyclohex-2-one and 7-oxabicyclo[4.1.0]heptan- 2-one. The product of 7-oxabicyclo[4.1.0]heptane-2-one is the first reported product through these process. All the oxidations were easily carried out. The factors that influence the oxidation were also well investigated. It can be concluded that the optimum reaction condition of the oxidation is: cyclohexene 5.0 ml, catalysts 2.0 mg, oxidant 1 atm molecular oxygen, 70 °C for 6 h. The promising kind of solvent as well as the volume of acidic additives would useful for the oxidation.

Acknowledgements

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