Formation of 2,6-Naphthalenedicarboxylic Acid by the Co–Mn–Br-Catalyzed Autoxidation of 2,6-Diethylnaphthalene in Acetic Acid

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In order to elucidate the reaction mechanism and the optimum reaction conditions for the formation of 2,6-naphthalenedicarboxylic acid (NDCA), the $Co(OAc)_2$–$Mn(OAc)_2$–NaBr-catalyzed oxidation of 2,6-diethylnaphthalene by molecular oxygen was carried out in acetic acid. The oxidation of the ethyl groups to carboxyl groups proceeded mainly via acetyl groups and partly via 1-hydroxyethyl and 1-acetoxyethyl groups. A synergistic catalytic effect due to Co and Mn acetates was observed not only on the rate of oxidation but also on the selective formation of NDCA. The rate of oxidation was strongly retarded at higher concentrations of the substrate, showing that the naphthalene nucleus terminates the chain reaction step of the oxidation. A high concentration of metal catalyst resulted in an increase of acetoxyethylnaphthoic acid. At the optimum reaction conditions, a nearly 90% yield of NDCA was obtained along with small amounts of substituted naphthoic and trimellitic acids. The differences in the yield of NDCA from 2,6-dimethyl, 2,6-diethyl, and 2,6-diisopropylnaphthalenes were compared under similar reaction conditions and are discussed.

Since 2,6-naphthalenedicarboxylic acid is an excellent component of high grade polyester,[1)] its synthetic process has been attracting much attention.

A mixture of dimethylnaphthalenes can be obtained from the middle distillate fractions of coal tar or light cycle oil of the catalytic cracking process, but separation of 2,6-dimethylnaphthalene from its isomers, especially from 2,7-dimethylnaphthalene, is very difficult because of very similar physical properties such as boiling and melting points.

Selective formation of 2,6-dimethylnaphthalene by alkylation of naphthalene or isomerization of dimethylnaphthalenes is not yet successful.

On the other hand, selective alkylation to form 2,6-diisopropylnaphthalene and separation from its isomers can be accomplished with very little difficulty.[2)]

However, the formation of the dicarboxylic acid from the oxidation of diisopropylnaphthalene is considerably more difficult than the dicarboxylic acid formation from dimethylnaphthalene because of strong inhibition and by-product formation in the course of oxidation of the isopropyl group on the naphthalene nucleus.[3,4)]

Generally, the $Co(OAc)_2$–$Mn(OAc)_2$–NaBr-catalyzed oxidation of alkylnaphthalenes is retarded by an aromatic nucleus. When the rate of oxidation is plotted against substrate concentration, the relation is generally bell-shaped[4)] in contrast to the first order relation of ordinary hydrocarbons such as alkylbenzenes.[5)]

Larsen et al.[6)] reported that at temperatures above 100 °C, alkylated naphthalenes were very significantly less reactive toward atmospheric oxygen than alkylated benzenes.

Recently, Igarashi et al.[7,8)] made clear that the addition of peroxyl radical to the naphthalene nucleus results in the formation of hydroperoxyl and naphthoxyl radicals, which terminate the autoxidation chain. The self-inhibiting reaction by the naphthalene nucleus was observed to be very low at 60 °C but considerably higher at 150 °C.

In this paper, we intended to clarify the overall oxidation scheme and features of the oxidation of the ethyl groups on the naphthalene nucleus as well as the optimum reaction conditions for the formation of 2,6-naphthalene dicarboxylic acid in the oxidation of 2,6-diethylnaphthalene with Co–Mn–Br catalyst, since the derivation of 2,6-diethylnaphthalene from naphthalene by the transalkylation was recently reported to be accomplished relatively easily.[9)]

Experimental

Materials: Acetic acid, metal acetates, and other materials were of reagent grade and were used without further purification. Sodium bromide was dried under vacuum at 150 °C for 5 h. 2-Ethylnaphthalene, 2,6-diethylnaphthalene, and other alkylnaphthalenes were of reagent grade and were used after distillation and recrystallization.

Procedure: A 100 mL autoclave made of Ti was used and the reaction was carried out by a batch method. After metal acetates, sodium bromide, and acetic acid (20 mL) were added to the autoclave, oxygen with 12 bar partial pressure was introduced from a gas cylinder without further purification, and the general reaction was carried out at 160 °C for 1 h.

The total pressure of the reaction was kept at a constant value of 15 bar in general, so the partial pressure of oxygen was 12 bar at the initial stage of the reaction at 160 °C, because the vapor pressure of acetic acid is 3 bar. The partial pressure of carbon dioxide and water was about 5 bar at the end of the reaction, when the oxidation proceeded almost completely as in the case of Run 35 in Table 2.

Some oxidations were carried out at 80 or 90 °C by using an ordinary 200 mL flask with a reflux condenser and an oxygen inlet.

The rate of oxygen uptake was measured continuously in an automatic recording gas absorption apparatus made of a pyrex glass ampoule under oxygen with a pressure transducer.

The oxidation products esterified by diazomethane were analyzed by gas chromatography on a Shimadzu model GC-8A with dual flame detectors using 4.2 m silicon OV-17 columns.

From the 2-ethylnaphthalene (EN) oxidation products, 2-acetylnaphthalene (AN), 2-(1-hydroxyethyl)naphthalene (HEN), 2-(1-acetoxyethyl)naphthalene (AEN), and 2-naphthoic acid (NCA) were isolated by column chromatography and identified by IR, ^{1}H NMR, and GC-MS. HEN was also separately synthesized by $\mathrm{LiAlH_4}$ hydrogenation of AN in THF.[10] AEN was derived by conventional esterification of HEN.

From the 2,6-diethylnaphthalene (DEN) oxidation products, 6-ethyl-2-naphthoic, 6-acetyl-2-naphthoic, 6-(1-acetoxyethyl)-2-naphthoic, trimellitic, and 2,6-naphthalenedicarboxylic acids (ENA, ANA, AENA, TMA, and NDCA) were isolated and identified by IR, ^{1}H NMR, and GC-MS.

Results and Discussion

1. Oxidation of Ethylnaphthalene. The time profile of the oxidation products from 2-ethylnaphthalene catalyzed by $\mathrm{Co(OAc)_2}$–$\mathrm{Mn(OAc)_2}$–NaBr at 90 °C is shown in Fig. 1. It is clear that the oxidation of EN proceeds to NCA via AN and HEN, and that the oxidation step of EN to AN proceeds quickly as compared to that of AN to NCA. Indeed, the rate of oxygen absorption by EN was observed to be several times faster than that by AN at 90 °C. AEN can be derived from the esterification of HEN by acetic acid and also from the reaction of the ethyl group with cobalt(III) acetate.[1] The oxidation of AEN seems relatively slow under these reaction conditions.

The rate of oxygen absorption by EN, which showed a maximum value at the initial stage, is plotted as a function of the Co/Mn molar ratio in Fig. 2. Cobalt and manganese were synergistic and the rate was highest at a Co/Mn molar ratio of 4/1 as in the case of ethylbenzene.[5]

The rate of oxidation of AN was very low compared with that of EN and showed a maximum value at a Co/Mn ratio of 2/3, suggesting that the synergistic catalytic effect by the metal acetates depends on the structure of the substrate.

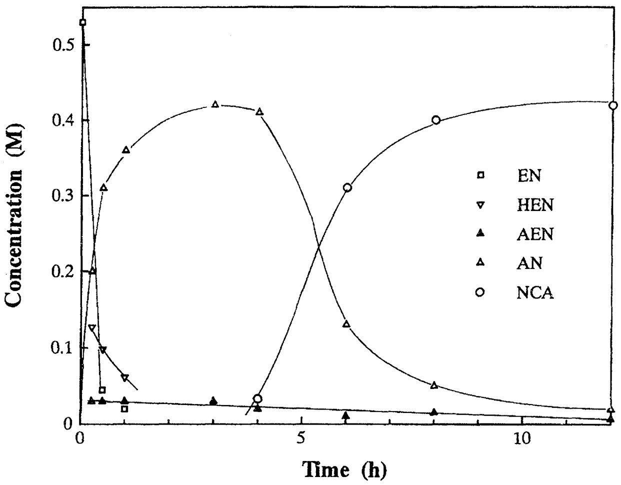

Fig. 1. Time profile of the products distribution in the Co–Mn–Br-catalyzed oxidation of 2-ethylnaphthalene in acetic acid at 90 °C. [Subst.]=0.53 M, (1 M=1 mol dm^{-3}), [Subst.] : [Metal] : [NaBr]=100 : 4 : 8, [Co] : [Mn]=1 : 1 (molar ratio), atmospheric oxygen.

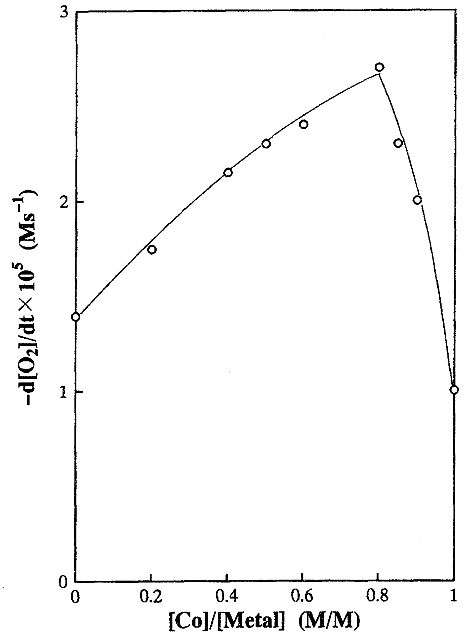

Fig. 2. Effect of catalyst composition in the Co–Mn–Br-catalyzed oxidation of 2-ethylnaphthalene in acetic acid at 90 °C. [Subst.] = 0.1 M, [Subst.] : [Metal] : [NaBr] = 100 : 10 : 20 (molar ratio), atmospheric oxygen.

Generally, the rates of oxidation of alkylbenzenes and alkylnaphthalenes have been reported to show a maximum value[3—5] at a NaBr/Metal catalyst molar ratio of 2. However, as seen in Fig. 3, the bromides of the transition metals were no more excellent catalysts in the oxidation of the acetyl group.

It should be mentioned that cobalt(III) or manganese(III) acetates are very good catalysts in the oxidation of carbonyl compounds.[12,13]

It was confirmed that in the oxidation of EN under

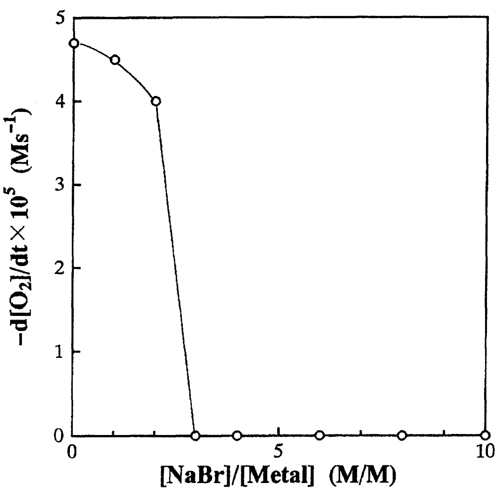

Fig. 3. Additive effect of bromide in the Co–Mn–Br-catalyzed oxidation of 2-acetylnaphthalene in acetic acid at 90 °C. [Subst.]=0.53 M, [Subst.] : [Metal]= 100 : 2, [Co] : [Mn]=1 : 1 (molar ratio), atomospheric oxygen.

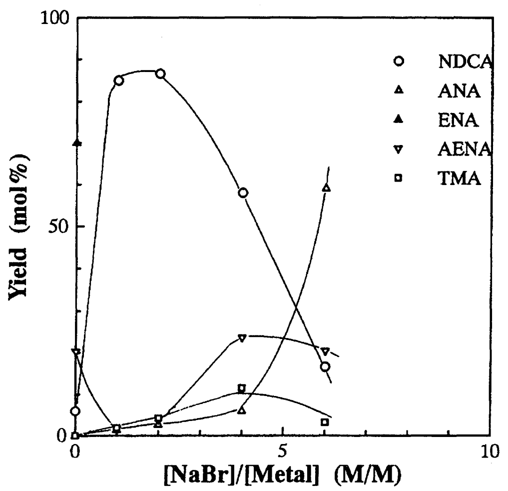

Fig. 5. Additive effect of bromide on the products distribution in the Co–Mn–Br-catalyzed oxidation of 2,6-diethylnaphthalene in acetic acid at 160 °C. [Subst.]=0.265 M, [Subst.] : [Metal]=100 : 30, [Co] : [Mn]=1 : 1 (molar ratio), O_2 press 12 bar, 1 h.

pressure at 150 °C, the yield of NCA was nearly 90% at Co/Mn ratios between 2/3 and 3/2.

As shown in Table 1, it was observed that the oxidation of AN proceeded rapidly only in the presence of a small amount of cobalt(III) salt, yielding an almost quantitative amount of NCA, and the catalytic effect of the transition metals was retarded by a six-fold concentration of bromide ion.

2. Oxidation of 2,6-Diethylnaphthalene. As shown in Table 2 and in Fig. 4, a nearly 90% yield of NDCA from DEN could be obtained at Co/Mn molar ratios between 1/4 and 4/1. In the case of neat manganese(II) acetate, not only was the rate of oxidation low, but also the yields of AENA and the scission product of the naphthalene nucleus, TMA, were relatively high.

In addition, in the case of neat cobalt(II) acetate, no NDCA was obtained and intermediate products such as ENA, AENA, and ANA along with TMA were obtained.

Under appropriate reaction conditions, ENA and ANA were almost completely reacted, but some amounts of AENA remained as a relatively stable intermediate against oxidation. The yield of TMA seemed to become higher with increasing reaction temperature.

The effect of bromide ion addition to the transition metals is shown in Fig. 5. The highest yield of NDCA was 87%, and the yield of NDCA decreased when the

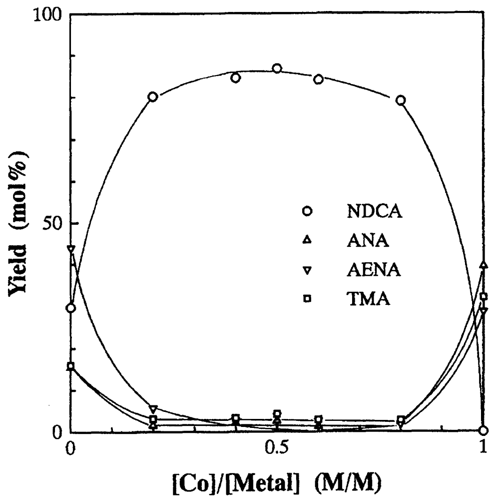

Fig. 4. Effect of catalyst composition on the products distribution in the Co–Mn–Br-catalyzed oxidation of 2,6-diethylnaphthalene in acetic acid at 160 °C. [Subst.]=0.265 M, [Subst.] : [Metal] : [NaBr]= 100 : 30 : 60 (molar ratio), O_2 press 12 bar, 1 h.

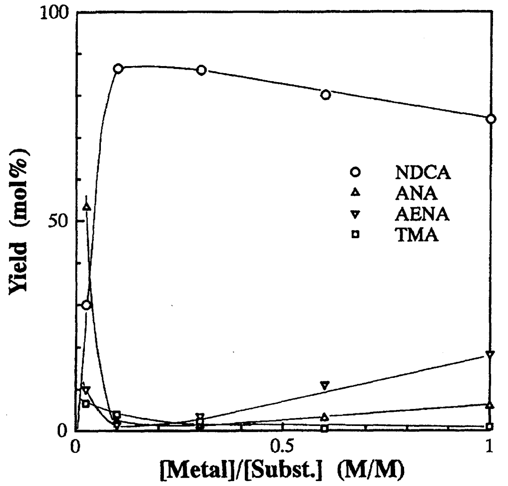

Fig. 6. Effect of catalyst concentration on the products distribution in the Co–Mn–Br-catalyzed oxidation of 2,6-diethylnaphthalene in acetic acid at 160 °C. [Subst.] = 0.265 M, [Co] : [Mn] : [NaBr] = 1 : 1 : 4 (molar ratio), O_2 press 12 bar, 1 h.

Table 1. Additive Effect of Bromide on the Products Distribution in the Co–Mn–Br- Catalyzed Oxidation of 2-Acetylnaphthalene [Subst.] : [Co+Mn]=10 : 1, [Co(II)+Co(III)] : [Mn(II)]=4 : 1, Co(III) : Tris(acetylacetonato)cobalt(III), [Subst.]=0.53 M, 1 M=1 mol dm^{-3}.

Run No.	Catalyst							O_2 Press	Temp	Time	Conv.	Products yield (mol%)		
	[Co(II)]	:	[Co(III)]	:	[Mn(II)]	:	[NaBr]	bar	°C	h	%	AN	NCA	OB[a)]
AN-1	8	:	—	:	2	:	20	7	150	10	0	100	0	0
2	72	:	8	:	20	:	200	7	150	7	100	0	94	0
5	16	:	4	:	5	:	—	7	150	1	100	0	93	0
6	16	:	4	:	5	:	50	7	150	1	100	0	94	1
7	16	:	4	:	5	:	25	7	150	1	100	0	95	0
8	16	:	4	:	5	:	150	7	150	4	0	100	0	0
9	16	:	4	:	5	:	150	7	150	24	100	0	92	0

a) Organic bromides.

Table 2. Effects of Reaction Condition on the Products Distribution in the Co–Mn–Br-Catalyzed Oxidation of 2,6-Diethylnaphthalene for 1 h

Run No.	[Subst.] / M	[Metal]	:	[NaBr]	:	[Subst.]	O_2 Press / bar	Temp / °C	Products yield (mol%)				
									ENA	ANA	NDCA	AENA	TMA
DEN-44	0.265	4	:	8	:	100	12	160	—	53	30	10	6
45	0.265	10	:	20	:	100	12	160	—	2	86	1	4
35	0.265	30	:	60	:	100	12	160	—	1	86	4	2
47	0.265	100	:	200	:	100	12	160	—	6	74	18	1
40	0.530	30	:	60	:	100	12	160	—	22	42	8	1
43	0.100	30	:	60	:	100	12	160	—	10	65	17	7
26	0.265	30	:	60	:	100	9	190	—	4	76	7	9
50	0.265	30	:	0	:	100	12	160	54	3	11	23	5
37	0.265	30	:	180	:	100	12	160	—	59	17	20	3
51	0.265	30	:	60	:	100	7	160	—	38	42	10	2
52	0.265	30	:	60	:	100	1	90	—	16	48	31	1
55	0.265	30	:	60	:	100	1	90	8	56	—	31	0

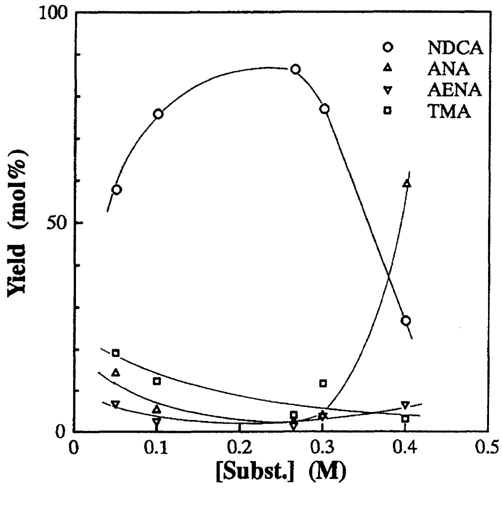

Fig. 7. Effect of substrate concentration on the products distribution in the Co–Mn–Br-catalyzed oxidation of 2,6-diethylnaphthalene in acetic acid at 160 °C at constant metal concentration of 0.0265 M. [Subst.] : [Metal] : [NaBr] = 100 : 30 : 60, [Co] : [Mn] = 1 : 1 (molar ratio), O_2 press 12 bar, 1 h.

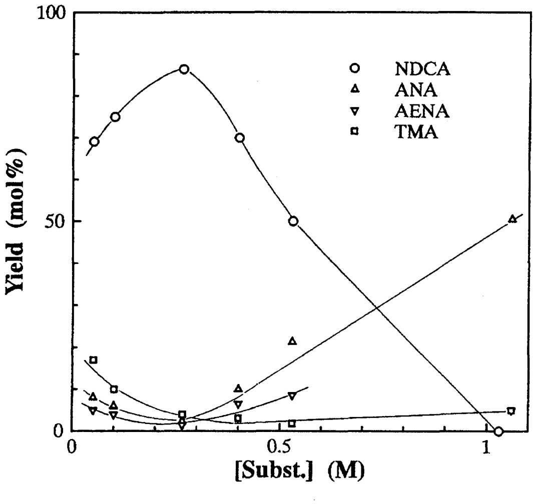

Fig. 8. Effect of substrste concentration on the products distribution in the Co–Mn–Br-catalyzed oxidation of 2,6-diethylnaphthalene in acetic acid at 160 °C at the substrate to metal catalyst molar ratio of 10/3. [Subst.] : [Metal] : [NaBr] = 100 : 30 : 60, [Co] : [Mn]=1 : 1 (molar ratio), O_2 press 12 bar, 1 h.

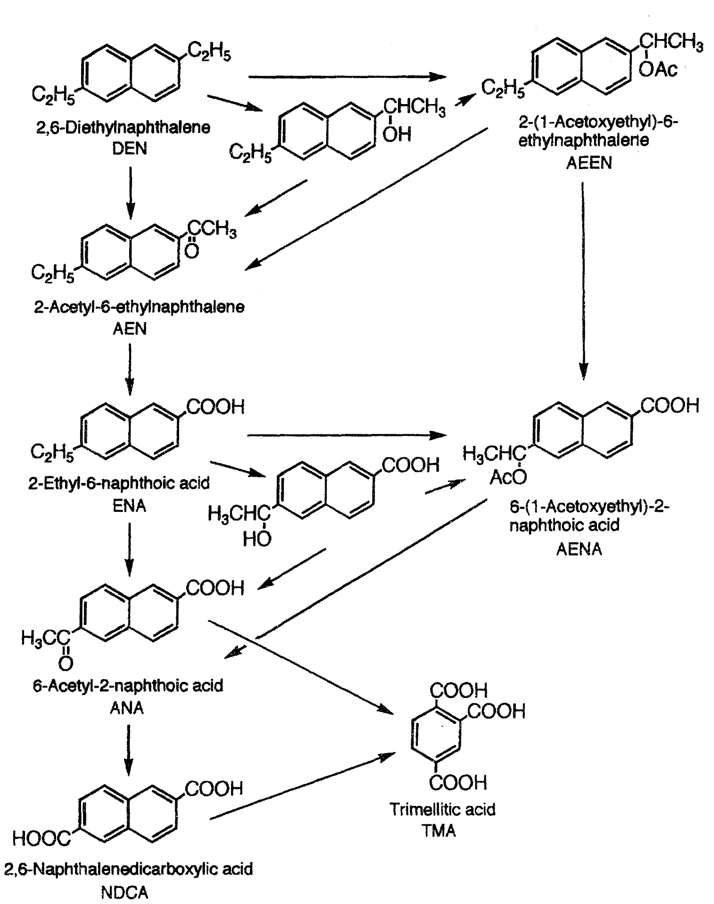

Fig. 9. Scheme of Co–Mn–Br-catalyzed oxidation of 2,6-diethylnaphthalene.

NaBr/Metal molar ratio was greater than 2/1.

These results indicate that the addition of an amount of sodium bromide greater than the amount of metal acetates is not effective and inhibits the oxidation step of DEN, in contrast to its effect in the oxidation of tetralin[14] and toluene.[5]

As shown in Fig. 6, the yield of NDCA showed the highest value at Metal/Substrate molar ratios between 0.1 and 0.3, and gradually decreased at higher ratios. This decrease corresponded to the formation of the relatively stable intermediates AENA and ANA.

As shown in Fig. 7, when the oxidation products were plotted as a function of the substrate concentration at a constant catalyst concentration, the yield of NDCA

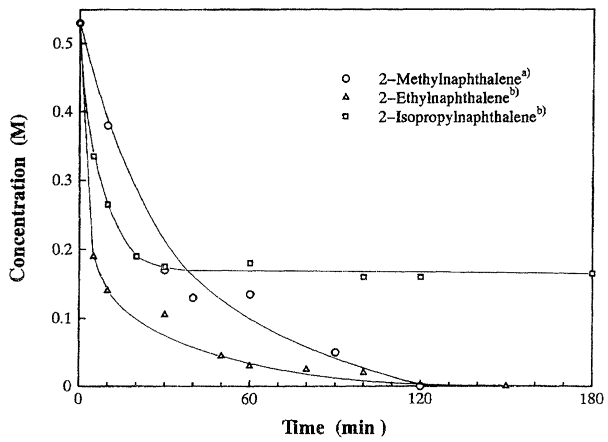

Fig. 10. Co–Mn–Br-catalyzed oxidation of 2-Methyl, 2-ethyl, and 2-isopropylnaphthalenes in acetic acid at 80 °C. [Subst.]=0.53 M, [Subst.] : [Metal] : [NaBr]= 100 : 4 : 8 (molar ratio), 1 h, atomospheric oxygen a) [Co] : [Mn]=4 : 1, b) [Co] : [Mn]=1 : 1 (molar ratio).

Table 3. Effect of Substrate Concentration on the Yield of 2,6-Naphthalenedicarboxylic Acid in the Co–Mn–Br-Catalyzed Oxidation of 2,6-Dialkylnaphthalenes (160 °C, 1 h, O_2 press 12 bar)

Subst.	[Subst.]	Catalyst	Yield
	M	Co : Mn : Br	mol%
2,6-Dimethylnaphthalene[a]	0.100	4 : 1 : 10	88
	0.265	4 : 1 : 10	87
	0.530	4 : 1 : 10	81
2,6-Diethylnaphthalene[a]	0.100	1 : 1 : 4	65
	0.265	1 : 1 : 4	87
	0.530	1 : 1 : 4	42
2,6-Diisopropylnaphthalene[b]	0.100	1 : 1 : 4	43
	0.265	1 : 1 : 4	29
	0.530	1 : 1 : 4	0

a) [Metal]/[Subst.]=0.3, b) [Metal]/[Subst.]=0.5.

Table 4. Comparison of Catalyst Concentration Effect on the Yield of 2,6-Naphthalenedicarboxylic Acid in the Oxidation of 2,6-Dialkylnaphthalenes (160 °C, 1 h, O_2 press 12 bar)

Subst.	[Subst.]	[Metal]/[Subst.]	[Cat.]	Yield
	M	molar ratio	Co : Mn : Br	mol%
2,6-Dimethylnaphthalene	0.265	0.04	4 : 1 : 10	75
	0.265	0.10	4 : 1 : 10	83
	0.265	0.30	4 : 1 : 10	88
	0.265	0.50	4 : 1 : 10	80
2,6-Diethylnaphthalene	0.265	0.04	1 : 1 : 4	30
	0.265	0.10	1 : 1 : 4	86
	0.265	0.30	1 : 1 : 4	86
	0.265	0.50	1 : 1 : 4	80
2,6-Diisopropylnaphthalene	0.100	0.50	1 : 1 : 4	43
	0.100	1.00	1 : 1 : 4	47
	0.100	2.00	1 : 1 : 4	50

showed a maximum value at a substrate concentration of 0.265 M (1 M=1 mol dm^{-3}), which corresponds to ten times the metal catalyst concentration. The yield remarkably decreased at higher substrate concentrations, showing that the rate of oxidation of DEN was suppressed strongly not only by the oxidation of the naphthalene nucleus, but also by metal catalyst deactivation due to oxidation products such as trimellitic acid, which is an effective chelating agent.

In order to compensate for the effect of metal catalyst deactivation, oxidation products were plotted against the substrate concentration at a constant Metal catalyst/Substrate molar ratio of 3/10 in Fig. 8. Again, this result clearly shows that the oxidation was strongly retarded by the reaction of the naphthalene nucleus with the chain-carrying active species.[15]

The scheme of Co–Mn–Br-catalyzed oxidation of 2,6-diethylnaphthalene is shown in Fig. 9.

3. Comparison of the Reactivity of Dimethyl-, Diethyl-, and Diisopropylnaphthalenes. In order to compare the reactivity of the alkyl substituents, oxidations of methyl-, ethyl-, and isopropylnaphthalenes were carried out under the same reaction conditions at 80 °C under atmospheric oxygen as shown in Fig. 10.

The oxidation of 2-methylnaphthalene proceeded slowly but steadily until the middle stage and finished after 120 min. The oxidation of 2-ethylnaphthalene proceeded most rapidly at the initial stage, but slowed down considerably at the late stage and was completed after 150 min.

In contrast, the oxidation of 2-isopropylnaphthalene proceeded rapidly at the initial stage, but became slow after 20 min and completely stopped at a conversion of 70%. Under these reaction conditions, no metal deactivators such as trimellitic acid were detected, but an appreciable amount of naphthol, an inhibitor of autoxidation, was detected in the oxidation products.

The above results can be compared with the yields of benzoic acid[16] from toluene, ethylbenzene, and isopropylbenzene, which are 88, 79, and 57%, respectively. The oxidation of the methyl group results in the formation of an aldehyde, which is a very reactive group in autoxidation and can accelerate the rate of the oxidation of methyl group.

On the other hand, the oxidation of an ethyl group results mainly in the formation of a more stable acetyl group as described above. As reported previously,[4] the oxidation of an isopropyl group also results in a stable acetyl group and may result in the formation of a small amount of inhibitive naphthol, probably due to acid-catalyzed decomposition of isopropyl hydroperoxide.

The yield of 2,6-naphthalenedicarboxylic acid from the oxidation of 2,6-dimethyl-, 2,6-diethyl-, and 2,6-diisopropylnaphthalenes (DMN, DEN, and DIPN) at 160 °C are compared in Table 3. In this case, the ratios of Co/Mn and Metal/Substrate were changed a little according to the substrate, and the concentration of substrate was kept below 0.53 M.

The oxidation of DMN proceeded most rapidly and showed an NDCA yield of 87%. In addition, the oxidation of DEN proceeded relatively easily with an NDCA yield of 87% at 0.265 M substrate concentration. In contrast, in the case of DIPN, the yield of NDCA was lower than 43% even at a higher catalyst concentration.

It can be concluded that oxidation of DIPN is most difficult because of the formation of many unfavorable by-products such as isopropenylnaphthalene and naphthol which result in retardation of the oxidation and a low NDCA yield.[4]

In Table 4, the yield of NDCA from three 2,6-dialkyl naphthalenes is compared at various ratios of metal catalyst to substrate. In the cases of DMN and DEN, a high yield of NDCA can be obtained at Metal/Substrate molar ratios between 0.1 and 0.3, but in the case of DIPN the yield of NDCA was lower than 50% even at a Metal/Substrate ratio of 1.0 at 160 °C.

Conclusion

The ethyl groups on the naphthalene nucleus were found to be converted to carboxyl groups mainly via acetyl groups in the $Co(OAc)_2$–$Mn(OAc)_2$–NaBr-catalyzed oxidation of 2,6-diethylnaphthalene by molecular oxygen, giving a nearly 90% yield of 2,6-naphthalenedicarboxylic acid at 160 °C after 1 h. The oxidation was synergistic with cobalt and manganese acetates in the presence of bromide ion. High concentrations of the metal catalyst tended to increase the yield of 6-(1-acetoxyethyl)-2-naphthoic acid.

As in the cases of other alkylnaphthalenes, the oxidation of 2,6-diethylnaphthalene was retarded by the naphthalene nucleus. The optimum concentration of substrate was suggested to be as low as 0.3 M.

In general, the oxidation of 2,6-diethylnaphthalene was found to proceed with much less difficulty than 2,6-diisopropylnaphthalene.

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References

1) I. Ouchi, H. Aoki, H. Shimotsuma, T. Asai, and M. Hosoi, "17th Japan Congress on Nonmetallic Materials, Proceedings," Kyoto, Japan, 1974, Abstr., p. 217.

2) Y. Sugi, *Fine Chem.*, **18**, 5 (1989).

3) Y. Kamiya, T. Taguchi, and S. Futamura, *Nippon Kagaku Kaishi*, **1987**, 1772.

4) Y. Kamiya, T. Kumakura, N. Hayashi, and H. Miyata, *Sekiyu Gakkaishi*, **36**, 15 (1993).

5) Y. Kamiya, *Adv. Chem. Ser.*, **76**, 193 (1968).

6) R. G. Larsen, R. E. Thorpe, and R. F. Armfield, *Ind. End. Chem.*, **34**, 183 (1942).

7) J. Igarashi, J. Lusztyk, and K. U. Ingold, *J. Am. Chem. Soc.*, **114**, 7719 (1992).

8) J. Igarashi, R. K. Jensen, J. Lusztyk, S. Korcek, and K. U. Ingold, *J. Am. Chem. Soc.*, **114**, 7727 (1992).

9) G. Takeuchi, N. Saito, Y. Shimomura, and K. Kariu, Japan Patent Laid Open No. 105639 (1993).

10) R. G. R. Bacon, R. G. Guy, and R. S. Irwin, *J. Chem. Soc.*, **1961**, 2436.

11) Y. Kamiya and M. Kashima, *Bull. Chem. Soc. Jpn.*, **46**, 905 (1973).

12) Y. Kamiya, *Kogyo Kagaku Zasshi*, **74**, 1811 (1971).

13) Y. Kamiya and M. Kotake, *Bull. Chem. Soc. Jpn.*, **46**, 2780 (1973).

14) Y. Kamiya, *Tetrahedron*, **22**, 2029 (1966).

15) Y. Kamiya, *J. Catal.*, **33**, 480 (1974).

16) D. E. Burney, G. H. Weisemann, and N. Fragen, *Petrol. Refiner*, **38**, 186 (1959).