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The Liquid-phase Oxidation of Hydrocarbons with Molecular Oxygen. II.[1) A Highly Selective Formation of α-Tetralone by the Metal-catalyzed Oxidation of Tetralin in the Presence of *N*,*N*-Dialkylamides

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The metal-ion catalyzed oxidation of tetralin was carried out in different solvents in which metal salts tend to be soluble. It was found that, for the production of α-tetralone, a chromium salt is the best catalyst among the first-transition-metal salts employed, while *N*,*N*-dialkylamides are the best solvents or the best additives. For example, in the tris(acetylacetonato)chromium(III)-catalyzed oxidation of tetralin in the presence of *N*,*N*-dimethylacetamide, α-tetralone was obtained in a 93.0% yield at a 27.2% tetralin conversion. The decomposition of α-tetralyl hydroperoxide (THP) with different first-transition-metal catalysts was also carried out in *N*,*N*-dimethylformamide in order to elucidate the formation mechanism for α-tetralone in the oxidation of tetralin in the presence of *N*,*N*-dialkylamides. It was concluded that the product distribution in the oxidation mainly depends on the decomposition mechanism of THP, and that *N*,*N*-dialkylamides seem to promote the reaction of the α-tetralylperoxyl radical with low valent metal ions, $ROO\cdot + M^{n+} \longrightarrow \alpha\text{-tetralone} + OH^- + M^{(n+1)+}$.

The dehydrogenation of α-tetralone is a commercial process for the production of α-naphthol.[2–4) α-Tetralone can be easily obtained by the liquid-phase autoxidation of tetralin, but in this oxidation α-tetralol is also produced in a large amount. α-Tetralol tends to undergo dehydration rather than dehydrogenation[5–7) and is unsuitable as a raw material for the production of α-naphthol. What is worse, the boiling point of α-tetralol is very close to that of α-tetralone. For these reasons, many investigations[6–12) have been undertaken in search of a method for the highly selective formation of α-tetralone in the autoxidation of tetralin. However, no satisfactory process for the production of α-tetralone has so far been found. In order to seek a better method of producing α-tetralone, we first studied the oxidation of tetralin in both the presence and absence of additives in acetic acid, using first-transition-metal salts as a catalyst. Chromium salts showed the highest ratio of α-tetralone/α-tetralol (ON/OL), while cobalt salts showed the highest activity in this tetralin oxidation. On the basis of this result, we further studied the effects of solvents and additives on the oxidation of tetralin; we thus found a satisfactory process for the production of α-tetralone by the liquid-phase oxidation of tetralin with molecular oxygen. This new process will now be reported in the present paper.

Experimental

Materials. The tetralin, metal salts, additives, and solvents employed were all of a reagent grade and were used without further purification. The α-tetralyl hydroperoxide (THP) was synthesized according to the procedure of Knight and Swern.[13) This peroxide was 97% pure, as confirmed by iodometric titration.

Oxidation of Tetralin. The oxidation of tetralin was performed in closed systems at higher pressures (a SUS-316 autoclave equipped with a magnetic stirrer, a thermocouple, and a pressure controller) and at atmospheric pressures (a 200 cm^3 three-necked flask equipped with a thermometer, a reflux condenser, an oxygen inlet, and a Teflon stirring bar).

A mixture of tetralin and a solvent or an additive containing a catalyst was placed in a reaction vessel and warmed to the desired temperature. Oxygen was then introduced into the vessel. However, in the oxidation under atmospheric pressure, the air in the vessel was quickly expelled by 600 cm^3 of oxgen in order to increase oxygen content in the reaction mixture when the temperature of the mixture had reached the desired temperature.

The oxidation was terminated by stopping the oxygen feed and by quickly cooling the vessel in an ice-cold bath.

Decomposition of THP. A four-necked flask (200 cm^3, round-bottomed) equipped with a thermometer, a reflux condenser, a dropping funnel, and a nitrogen inlet was filled with nitrogen gas. Into the flask, were placed a Teflon stirring bar and a 50 cm^3 solution of *N*,*N*-dimethylformamide (DMF) containing a catalyst. A stream of nitrogen was gently bubbled through the solution. The solution was then stirred and warmed to the desired temperature. To the vigorously stirred solution, was added a 25 cm^3 solution of DMF containing 2.5 g of THP.

Analysis. The peroxide concentration was determined by the usual method.[14) The α-tetralone, α-tetralol, and tetralin in the reaction mixture were identified and their amounts were determined using gas chromatography with a Shimadzu GC-4CPT chromatograph (2 m × 3 mm column packed with 10% Carbowax 4000 on Chromosorb AW; programming, 5 °C/min from 120 to 173 °C, He 40 cm^3/min). *o*-Bromoanisole was used as the internal standard. Before GLC analysis, the remaining peroxide was reduced with an excess of triphenylphosphine.[15) The "net α-tetralol" is the difference between the total amount of α-tetralol after reduction and the amount of peroxide before reduction.

Results

The best conditions for producing α-tetralone in the liquid-phase oxidation of tetralin were examined using cobalt and chromium salts as catalysts.

The Selection of Solvents. The $Co(C_6H_5COO)_2$-catalyzed oxidation of tetralin under an atmospheric pressure at 51 °C was carried out in different solvents in which metal salts tend to be soluble. The results are shown in Table 1. Tetralin was almost not oxidized at all in either dimethyl sulfoxide or tetrahydrothiophene 1,1-dioxide for 3 h. Although DMF brought a very high yield of peroxide, DMF gave by far the highest ON/OL ratio and the lowest α-tetralol yield among the solvents listed in Table 1.

The Determination of the Catalyst Concentration and Reac-

TABLE 1. PRODUCT DISTRIBUTION FOR THE COBALT-CATALYZE OXIDATION OF TETRALIN IN DIFFERENT SOLVENTS UNDER ATMOSPHERIC PRESSURE

Run No.	Solvent	Tetralin conversion %	Yield[a]/mol%				ON/OL	Reaction time min
			α-Tetralone	α-Tetralol	Peroxide	Total		
1	Acetic acid	19.4	27.0	37.2	14.5	78.7	0.73	126
2	Propionic acid	25.6	32.4	37.1	16.8	86.3	0.87	207
3	Acetonitrile	27.3	39.7	12.3	44.7	96.7	3.2	164
4	Propionitrile	25.3	32.4	9.1	41.6	83.1	3.6	237
5	Ethyl acetate	20.7	28.7	12.7	48.9	90.3	2.3	287
6	Acetic anhydride	31.8	33.7	28.3	0.3	62.3	1.2	245
7	Dioxane	22.3	24.0	2.8	63.1	89.9	8.6	250
8	DMF	21.9	32.7	1.4	56.1	90.2	23	175
9	Dimethyl sulfoxide	$\simeq 0.0$	—	—	—	—	—	180
10	Tetrahydrothiophene 1,1-dioxide	$\simeq 0.0$	—	—	—	—	—	180

Reaction conditions: $[\mathrm{Co(C_6H_5COO)_2}]=2.8\times10^{-3}$ M, $[\text{tetralin}]_{\text{initial}}=3.88$ M, the reaction temperature was 51±1 °C. a) Based on the amount of tetralin consumed.

TABLE 2. PRODUCT DISTRIBUTION FOR THE TRIS(ACETYLACETONATO)CHROMIUM(III)-CATALYZED OXIDATION OF TETRALIN IN DMF

Run No.	Catalyst $[\mathrm{Cr(acac)_3}]$ M	Initial [tetralin] M	Reaction temperature °C	Tetralin conversion %	Yield[a]/mol%				Reaction time min
					α-Tetralone	α-Tetralol	Peoxide	Total	
11	0.0266	3.85	140—218	33.9	54.2	16.6	3.0	73.8	2.5
12	0.0266	3.85	120—128	34.5	77.1	9.4	3.0	89.5	30
13	0.0266	3.85	100±1	32.2	80.5	7.8	2.0	90.3	150
14	0.0060	3.90	90±1	23.5	79.5	5.7	5.4	90.6	140
15	0.0238	7.25	130±1	43.8	70.9	8.5	8.3	87.7	30
16	0.0010	7.25	100±2	38.4	65.4	−1.2	26.1	90.3	90
17	0.0030	6.12	72±1	18.5	90.7	2.1	4.7	97.5	450
18	0.0053	5.76	100±1	39.6	83.5	3.5	3.7	90.7	150
19	0.0106	5.76	100±2	39.2	83.9	4.8	3.4	92.1	100
20	0.0265	5.74	100±2	34.7	86.5	7.6	3.5	97.6	66

Reaction conditions: the O_2 pressure was 20 kg/cm^2 G. a) Based on the amount of tetralin consumed.

TABLE 3. PRODUCT DISTRIBUTION FOR THE OXIDATION OF TETRALIN CATALYZED BY DIFFERENT CHROMIUM SALTS IN THE PRESENCE OF DMF

Run No.	Catalyst	Reaction temperature °C	Tetralin conversition %	Yield[a]/mol%				Reaction time min
				α-Tetralone	α-Tetralol	Peroxide	Total	
21	$\mathrm{Cr(acac)_3}$	110±1	30.1	79.1	6.5	5.3	90.9	51
22	$\mathrm{Cr(OAc)_3}$	109±2	28.9	80.8	5.8	4.9	91.5	70
23	$\mathrm{Cr(NO_3)\cdot 9H_2O}$	110±2	30.1	81.3	4.9	4.3	90.5	120
24	$\mathrm{CrCl_3\cdot 6H_2O}$	100—120	29.3	76.5	7.2	5.9	89.6	22
25	$\mathrm{CrF_3\cdot 3H_2O}$	110±1	29.8	74.1	3.3	13.6	91.0	130
26	$\mathrm{Cr(OH)_3}$	110±1	29.3	80.4	4.6	5.3	90.3	105
27	$\mathrm{Cr_2(SO_4)_3}\cdot x\mathrm{H_2O}$	110±1	31.3	76.2	2.7	9.7	88.6	115
28	3% Cr-naphthenate	110±2	29.3	75.7	9.7	4.8	90.2	48
29	$\mathrm{Cr_2O_3}$	110±1	29.9	61.5	2.4	26.9	90.8	320

Reaction conditions: $[\mathrm{Cr}]=6.0\times10^{-3}$ M, $[\text{tetralin}]_{\text{initial}}=4.90$ M; the O_2 pressure was 20 kg/cm^2 G. a) Based on the amount of tetralin consumed.

Table 4. Product distribution for the bis(acetylacetonato)cobalt(II)-catalyzed oxidation of tetralin in the presence of additives in DMF

Run No.	Additive	Reaction temperature °C	Tetralin conversion %	Yield[a)]/mol%				Reaction time min
				α-Tetralone	α-Tetralol	Peroxide	Total	
30	—	72.5±1	23.1	73.5	14.6	5.6	93.7	60
31	KSCN	72.5±1	32.1	72.4	16.2	3.2	91.8	100
32	NaNO$_2$	71—75	21.1	76.7	13.3	5.0	95.0	120
33	LiBr	72.5±1	23.3	72.6	15.0	3.8	91.4	60

Reaction conditions; [Co(acac)$_2$] = [additive] = 1.06×10^{-2} M; the O$_2$ pressure was 20 kg/cm^2 G, $[\text{tetralin}]_{\text{initial}}$ = 3.85 M. a) Based on the amount of tetralin consumed.

Table 5. Product distribution for the oxidation of tetralin catalyzed by different transition-metal salts in DMF

Run No.	Catalyst Metal salts	Catalyst Concn 10^3 M	Initial [tetralin] M	React. temp °C	Tetralin conv. %	Yield[a)]/mol%				ON/OL	Reaction time min	Maximum rate of O$_2$ absorption 10^3 mol min^{-1}
						α-Tetralone	α-Tetralol	Peroxide	Total			
34	Cr(acac)$_2$	6.0	3.90	90±1	23.5	79.5	5.7	5.4	90.6	14	143	2.5
35	CrCl$_3$·6H$_2$O	6.0	3.92	90±2	18.5	71.4	9.9	6.8	88.1	7.2	240	1.0
36	Cr(OAc)$_3$	6.0	3.91	90±1	28.1	78.6	4.6	5.9	89.1	17	111	3.3
37	Mn(OAc)$_2$·4H$_2$O	6.0	3.92	90±2	18.2	56.0	21.7	3.4	81.1	2.6	240	2.3
38	FeCl$_3$	6.0	3.93	90±1	26.2	63.5	7.3	15.6	86.4	8.7	223	1.2
39	Co(OAc)$_2$·4H$_2$O	6.0	3.92	90±2	21.6	68.5	18.0	≃0.0	86.5	3.8	240[b)]	14
40	Ni(OAc)$_2$·4H$_2$O	6.0	3.89	90±1	24.6	53.4	≃0.0	37.8	91.2	—	240[b)]	4.5
41	Cu(OAc)$_2$·H$_2$O	6.0	3.90	90±2	7.3	70.3	19.0	0.9	90.2	3.7	240[b)]	4.3
42	Cr(acac)$_3$	6.0	6.10	90±1	26.0	84.9	5.1	3.5	93.5	17	105	4.0
43	Ni(OAc)$_2$·4H$_2$O	6.0	6.13	90±1	25.0	72.4	3.0	18.4	93.8	24	180	5.3
44	Co(OAc)$_2$·4H$_2$O	6.0	3.91	65±1	28.5	72.6	14.7	6.9	94.2	4.9	73	3.8
45	Co(OAc)$_2$·4H$_2$O	3.0	3.90	90±2	27.4	74.4	18.8	≃0.0	93.2	4.0	40	13
46	Co(OAc)$_2$·4H$_2$O	3.0	3.91	65±1	28.0	53.8	2.8	37.2	93.8	19	80	2.8

Reaction conditions: the O$_2$ pressure was 20 kg/cm^2 G. a) Based on the amount of tetralin consumed. b) The O$_2$ absorption rate fell suddenly about 20 min after the introduction of oxygen.

tion Temperature. Table 2 shows the effects of the catalyst concentration and the reaction temperature on the product distribution in the Cr(acac)$_3$-catalyzed oxidation of tetralin in DMF. The α-tetralone yield decreased with an increase in the reaction temperature (Runs 11—13). At reaction temperatures above 120 °C, it was also difficult to carry out the oxidation of tetralin at an approximately constant temperature. Accordingly, the optimum reaction temperatures for producing α-tetralone in the Cr(acac)$_3$-catalyzed oxidation of tetralin in the presence of DMF seem to be below 120 °C.

It was seen from Runs 18—20 that, at catalyst concentrations above 5×10^{-3} M**, the product distribution in the oxidation of tetralin is almost not at all dependent on the catalyst concentration, and all the α-tetralone yields obtained in these three runs are above 83%. A high α-tetralone yield was also obtained in the oxidation at the 3×10^{-3} M Cr(acac)$_3$ concentration, although the oxidation rate was very slow (Run 17). However, in the oxidation at the 1×10^{-3} M Cr(acac)$_3$ concentration, the peroxide yield was relatively high and the α-tetralone yield was relatively low (compare Run 15 with Run 16). Therefore, the best region of catalyst concentrations for the selective formation of α-tetralone appears to be $10^{-3}\,\mathrm{M}<[\mathrm{Cr}]\leqq10^{-2}\,\mathrm{M}$ in the Cr(acac)$_3$-catalyzed oxidation of tetralin in the presence of DMF.

The Effects of Ligands and Additives. Table 3 shows the oxidation of tetralin with nine kinds of chromium catalysts in DMF. Chromium(III) oxide, which is insoluble in a mixed solution of DMF and tetralin, showed a low α-tetralone yield and a very high peroxide yield in comparison with the other Cr catalysts. However, all the other Cr catalysts which are more or less soluble in the reaction mixture gave high α-tetralone yields (above 74%) and showed similar product distributions, although their oxidation activities were considerably different from each other. Such a phenomenon was also observed for the Co(acac)$_2$-catalyzed oxidation of tetralin in DMF in both the presence and absence of an additive, as is shown in Table 4. The four product distributions were very similar to each other (Runs 30—33). It was thus found that, for the tetralin oxidation in the presence of the appropriate amount of DMF, the counter anions and additives employed have much influence on the oxidation rate, but almost none on the product distribution. This fact seems to indicate that the counter anions and additives do not alter the oxidation mech-

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** 1 M = 1 mol dm^{-3}.

Table 6. Product distribution for the tris(acetylacetonato)chromium(III)-catalyzed oxidation of tetralin in the presence of *N*,*N*-dialkylamides

Run No.	Additive	Tetralin conversion %	Yield$^{a)}$/mol% α-Tetralone	α-Tetralol	Peroxide	Total	Reaction time min	Maximum rate of O_2 absorption 10^3 mol min^{-1}
47	DMF	28.1	84.7	2.0	4.0	91.6	285	1.4
48	DMA	29.5	85.5	5.8	2.8	94.1	88	15
49	DMP	30.0	88.4	1.2	3.2	92.8	198	2.8
50	DEF	28.1	82.1	5.2	5.2	92.5	240	2.8
51	DEA	29.9	89.0	1.4	3.9	94.3	183	5.3

Reaction conditions: $[Cr(acac)_3]=2.0\times10^{-3}$ M; $[tetralin]_{initial}=6.12$ M; the reaction temperature was 80±1 °C; the O_2 pressure was 20 kg/cm^2 G. DMA: $(CH_3)_2NCOCH_3$, DMP: $(CH_3)_2NCOC_2H_5$, DEF: $(C_2H_5)_2NCOH$, DEA: $(C_2H_5)_2NCOCH_3$. a) Based on the amount of tetralin consumed.

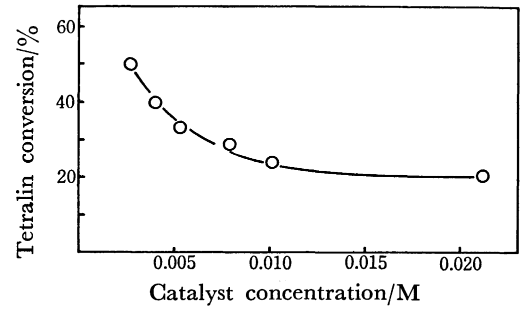


Fig. 1. Relationship between the catalyst concentration and the tetralin conversion in the $Co(acac)_2$-catalyzed oxidation of tetralin in DMF at 72±2 °C. Reaction conditions: $[tetralin]_{initial}=3.85$ M, the O_2 pressure was 20 kg/cm^2 G.

anism of tetralin, but the solubilities of metal (Co or Cr) catalysts and the ligand-replacement rates of active metal complexes in the reaction solution.

The Effects of Metal Ions. The effects of different first-transition-metal ions on the oxidation of tetralin in DMF are shown in Table 5. Chromium catalysts showed the highest α-tetralone yields among the catalysts employed and showed relatively high ON/OL ratios. Iron and Ni catalysts also showed high ON/OL ratios, but they also gave quite high peroxide yields. On the other hand, Mn, Co, and Cu catalysts were more favorable for producing α-tetralol than Cr, Ni, and Fe. Therefore, chromium salts are the best catalysts for producing α-tetralone in the oxidation of tetralin.

As can be seen from Runs 39—41 in Table 5, Co showed the highest activity, and Ni and Cu showed quite high activities, but these activities fell suddenly twenty minutes after the introduction of oxygen. This phenomenon was examined in detail for the oxidation of tetralin with Co catalysts, and it was observed that the tetralin conversion decreases with an increase in the Co concentration or the reaction temperature (Fig. 1 or Runs 39 and 44 in Table 5). This is thought to be due to the action of autoxidation inhibitors generated in consecutive oxidations, because the primary oxidation products of tetralin are easily oxidized with an increase in the Co concentration and in the reaction temperature. Actually, Martan *et al.*[16] have isolated α-naphthol and 1,4-dihydroxynaphthalene, both inhibitors, as higher products in the oxidation of tetralin catalyzed by $Co(OAc)_2$.

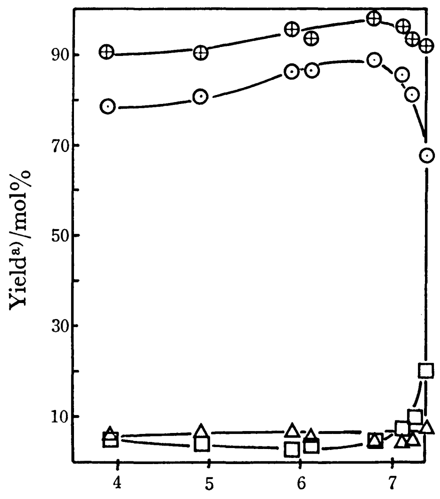


Fig. 2. The $Cr(acac)_3$-catalyzed oxidation of tetralin in DMF at 90±2 °C. Reaction conditions: $[Cr(acac)_3]=6.0\times10^{-3}$ M, the O_2 pressure was 20 kg/cm^{2}G, the tetralin conversion was 26.0±2.5%. ⊙: Tetralone, △: α-tetralol, □: peroxide, ⊕: total. a) Based on the amount of tetralin consumed.

The Effects of the Initial Tetralin Concentration. Figure 2 shows the dependence of the product distributions on the initial substrate concentration in the oxidation of tetralin catalyzed by $Cr(acac)_3$ in the presence of DMF at 90 °C. The right end of the abscissa in Fig. 2 indicates a neat tetralin solution without DMF. At initial tetralin concentrations above 7 M, the α-tetralone yield decreased suddenly and the peroxide yield increased rapidly with an increase in the tetralin concentration, although the α-tetralol yield was almost independent of the initial substrate concentration. At initial tetralin concentrations below 6.8 M, the α-tetralone yield decreased slowly upon a decrease in the tetralin concentration. From these facts and the solubility of $Cr(acac)_3$, the optimum region of initial tetralin concentration for producing α-tetralone seems to be 5.5—6.5 M in the oxidation of tetralin catalyzed by $Cr(acac)_3$ in the presence of DMF.

The Oxidation of Tetralin in the Presence of Different Amides and Oxygen Pressure. Table 6 shows the oxidation of tetralin catalyzed by $Cr(acac)_3$ in the presence of five kinds of *N*,*N*-dialkylamides at 80 °C,

Table 7. Effect of oxygen pressure on the tris(acetylacetonato)chromium(III)-catalyzed oxidation of tetralin in the presence of DMA

Run No.	O_2 pressure kg cm^{-2}G^{-1}	Catalyst concentration 10^3 M	Reaction temperature °C	Tetralin conversion %	Yield$^{a)}$/mol%				Reaction time min	Maximum rate of O_2 absorption 10^3 mol min^{-1}
					α-Tetralone	α-Tetlalol	Peroxide	Total		
52	20	3.0	80±3	28.9	84.2	6.2	2.8	93.2	87	16
53	10	3.0	80±1	41.7	88.3	≃0.0	4.5	92.8	260	4.7
54	2.5	3.0	80±1	27.2	93.0	0.5	1.6	95.1	270	2.0
55	20	2.0	80±1	29.5	85.5	5.8	2.8	94.1	88	15
56	6	2.0	80±2	31.2	89.3	1.7	3.3	94.3	147	5.8

Reaction conditions: $[\text{tetralin}]_{\text{initial}}=6.12$ M. a) Based on the amount of tetrain consumed.

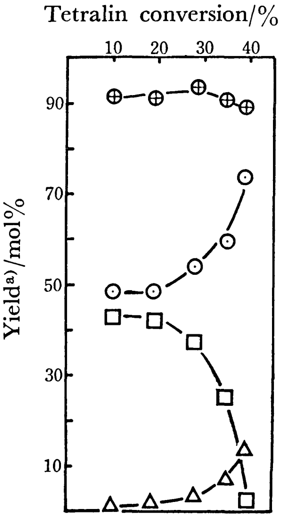


Fig. 3. The $Co(OAc)_2 \cdot 4H_2O$-catalyzed oxidation of tetralin in DMF at 65±2 °C. Reaction conditions: $[Co(OAc)_2 \cdot 4H_2O]=3.0\times10^{-3}$ M, $[\text{tetralin}]_{\text{initial}}=3.91$ M, the O_2 pressure was 20 kg/cm^2 G. ⊙: α-Tetralone, △: α-tetralol, □: peroxide, ⊕: total. a) Based on the amount of tetralin consumed.

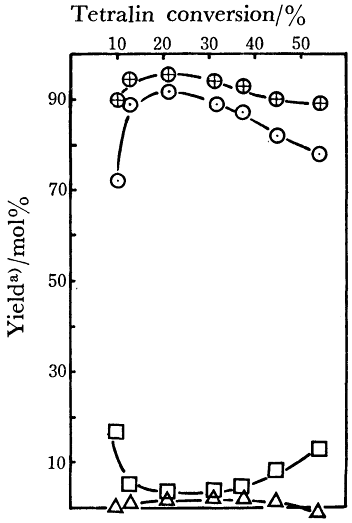


Fig. 4. The $Cr(acac)_3$-catalyzed oxidation of tetralin in the presence of DMA at 80±2 °C. Reaction conditions: $[Cr(acac)_3]=2.0\times10^{-3}$ M, $[\text{tetralin}]_{\text{initial}}=6.12$ M, the O_2 pressure was 6 kg/cm^2 G. ⊙: α-Tetralone, △: α-tetralol, □: peroxide, ⊕: total. a) Based on the amount of tetralin consumed.

All these amides brought about high α-tetralone yields and product distributions very similar to one another; that is, we could observe almost no substituent effect of these amides on the product distribution, although these amides had much influence on the oxidation rate of tetralin. Table 7 shows the effect of the oxygen pressure on the oxidation of tetralin in the presence of *N*,*N*-dimethylacetamide (DMA), which gave the highest oxidation rate among the amides employed. The oxidation rate of tetralin fell with a decrease in the oxygen pressure. This indicates that, at oxygen pressures below 20 kg/cm^2 G, the oxidation rate depends on the concentration of molecular oxygen in a mixed solution of DMA and tetralin. Accordingly, the differences between the oxygen absorption rates listed on Table 6 appear to be attributable mainly to the differences between the solubilities of oxygen in mixed solutions of different amides and tetralin. For the tetralin oxidation in the presence of *N*,*N*-dialkylamides (Runs 47—56), the recoveries of these amides ranged from 93 to 98%. Tetralin was also oxidized with molecular oxygen in the presence of acetamide at 95 °C under atmospheric pressure ($[\text{tetralin}]_{\text{initial}}=$ 6.12 M). This oxidation stopped at about a 10% tetralin conversion (the α-tetralone, α-tetralol, and peroxide yields are 47.3, 2.0 and 7.0% respectively), and the recovery of acetamide in this run was very low. This acetamide reactivity seems to come from the property[17—19] that primary and secondary amides can easily liberate their amino protons.

The Time-course of the Product Distributions. The product formation for different tetralin conversions was examined in the oxidation of tetralin catalyzed by $Co(OAc)_2 \cdot 4H_2O$ in DMF at 65 °C (Fig. 3). The yields of both α-tetralone and α-tetralol increased with an increase in the tetralin conversion; on the contrary, the peroxide yield decreased as the tetralin conversion increased. The total amount of the increment in the α-tetralone yield and that in the α-tetralol yield was nearly equal to the decrement in the peroxide yield. The increment in the α-tetralone yield was appreciably more than that in the α-tetralol yield. Accordingly, THP seems to be preferentially converted into α-tetralone, although THP decomposes to both α-tetralone and α-tetralol.

The product formation for various tetralin conversions was also examined in the $Cr(acac)_3$-catalyzed oxidation of tetralin in the presence of DMA at 80 °C

TABLE 8. PRODUCT DISTRIBUTION FOR THE METAL-CATALYZED DECOMPOSITION OF THP IN DMF IN A NITROGEN ATOMOSPHERE

Run No.	Metal salt	THP conversion %	Yield[a)]/mol% α-Tetralone	Yield[a)]/mol% α-Tetralol	ON/OL	Reaction time min
57	$Cr(OAc)_3$	87.9	85.3	6.2	14	210
58	$Mn(OAc)_2\cdot 4H_2O$	97.6	54.7	27.0	2.0	50
59	$FeCl_3$	99.2	79.2	15.0	5.3	15
60	$Co(acac)_2$	96.7	69.9	21.7	3.2	20
61	$Ni(OAc)_2\cdot 4H_2O$	96.6	93.0	$\simeq 0.0$	—	15
62	$Cu(OAc)_2\cdot H_2O$	98.5	81.6	9.5	8.6	15

Reaction conditions: [metal salt] $= 6.0 \times 10^{-3}$ M; $[THP]_{initial} = 0.20$ M; the reaction temperature was 71—75 °C.
a) Based on the amount of THP converted.

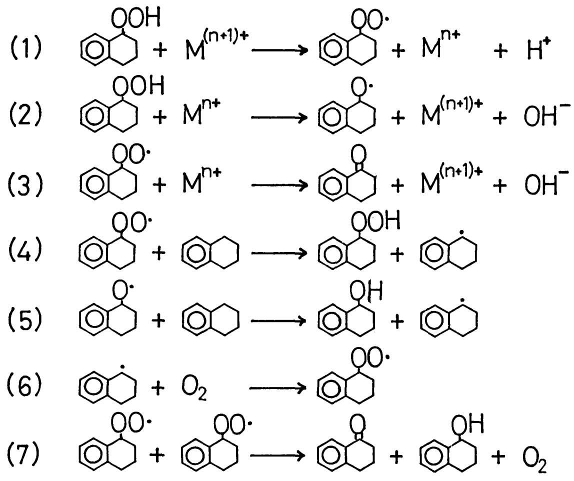
(Fig. 4). For tetralin conversions below 25%, the percentage of the decrease in the peroxide yield was nearly equal to that of the increase in the α-tetralone yield, and α-tetralol was only produced in a very low yield below 2%. This seems to show that the THP generated by the tetralin oxidation is converted almost exclusively into α-tetralone. On the other hand, for tetralin conversions above 25%, the α-tetralone yield decreased and the peroxide yield increased as the tetralin conversion was increased. The α-tetralol yield also had a minus sign for tetralin conversions above 50%. These facts suggest that the α-tetralone produced in the oxidation is further oxidized into a peroxide different from THP during the prolonged reaction time. Accordingly, in order to obtain α-tetralone in a high purity and a high yield, the $Cr(acac)_3$-catalyzed oxidation of tetralin in the presence of DMA should be stopped at 20—30% tetralin conversions.

The Decomposition of THP. The decomposition of THP with six kinds of first-transition-metal catalysts was carried out in DMF 71—75 °C in a nitrogen atmosphere. The ON/OL ratios decreased in this order: Ni>Cr>Cu>Fe>Co>Mn, as is shown in Table 8. This order is fully consistent with that of the decreasing reduction potentials[20–22] for these low-valent metal ions. In the oxidation of tetralin shown in Table 5, the ON/OL ratios decreased in this order: Ni>Cr>Fe>Co≃Cu>Mn. This order is inconsistent with that in the THP decomposition. However, except for the Cu catalyst, which gave too low a tetralin conversion in the oxidation (Run 41 in Table 5), the decreasing order of ON/OL ratios in the oxidation is in fair agreement with that in the THP decomposition. In addition, the product distributions in the decomposition of THP with six kinds of transition-metal catalysts are similar to those in the corresponding oxidation of tetralin. Accordingly, the product distribution in the tetralin oxidation is thought to depend mainly on the decomposition mechanism of the THP produced in the oxidation.

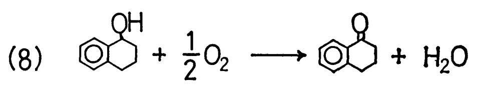
Discussion

The liquid-phase oxidation of tetralin has been widely studied, and the following elementary reactions (Eqs. 1—7) have been proposed in previous reports.[1,16,23–30] Equations 1—3 are elementary reactions involving metal ions. From Eqs. 1—3, two kinds of regeneration mechanisms of metal ions can be derived; one (the A-mechanism) is composed of Reactions 1 and 2, and the other (the B-mechanism), of Reactions 1 and 3.[31] The A-mechanism is the so-called Haber-Weiss mechanism[32–35] and is much more common as a regeneration mechanism of metal ions than the B-mechanism.

If metal ions catalyze both the tetralin oxidation and the THP decomposition by only the A-mechanism, α-tetralol will be produced in a higher yield than α-tetralone, as can be seen from Reactions 4—7, which follow Reactions 1 and 2. For most runs in the present work, however, the α-tetralol yields were lower than the α-tetralone yields. Although α-tetralol resulting from the tetralin oxidation can be converted into α-tetralone according to Reaction 8, Reaction 8 contributes almost nothing to the formation of α-tetralone in the oxidation of tetralin in the presence of *N,N*-dialkylamides, as can be seen from Figs. 3 and 4. Also, α-tetralone was always the main product in the decomposition of THP with six kinds of first-transition-metal catalysts in DMF under a nitrogen atmosphere. This fact cannot be explained by only the A-mechanism. On the other hand, if the B-mechanism contributes



Regeneration Mechanisms of Metal Ions
A:(1),(2) B:(1),(3)



only to the regeneration of metal ions, the main products in both the tetralin oxidation and the THP decomposition will be α-tetralone. However, for the oxidation of tetralin in aliphatic acids, the α-tetralol yields were higher than the α-tetralone yields, as is shown in Table 1. Accordingly, it seems reasonable to assume that the regeneration of metal ions actually proceeds by both mechanisms, A and B, with A or B predominating according to the reaction conditions.

As is shown in Tables 1 and 6, DMF brought about relatively a very high ON/OL ratio and in the presence of *N,N*-dialkylamides α-tetralone was produced in a very high yield. These facts suggest that, in the presence of *N,N*-dialkylamides, the B-mechanism rather than the A-mechanism performs the regeneration of metal ions. The predominance of the B-mechanism is further strengthened by the simultaneous use of highly reductive metal catalysts and *N,N*-dialkylamides, as can be seen from Tables 5 and 8. However, the actions of *N,N*-dialkylamides for the selective formation of α-tetralone cannot be interpreted explicitly at present. If *N,N*-dialkylamides promote Reaction 1 and suppress Reaction 2, Reaction 3 will be remarkably accelerated by highly reductive metal ions such as Cr^{2+}, and such metal catalysts will give high ON/OL ratios and high α-tetralone yields. It has been reported that *N,N*-dialkylamides have high hydrogen-bonding abilities[36] and DMF forms electron-donor-acceptor complexes[37] with halo hydrocarbons with acceptor properties. It was also observed in the present work that, when THP is dissolved in a solution of *N,N*-dialkylamides, the solution turns pale pink. Accordingly, the association between THP and *N,N*-dialkylamides may promote Reaction 1 and may inhibit Reaction 2. Furthermore, the absorption spectra of the DMF complexes of Cr(III)[38] show that DMF has a ligand-field strength comparable to that of the SCN^- ligand, which occupies a higher position in the spectrochemical series[39,40] than the H_2O, RCO_2^-, ROOH ligands. Compared with ligands such as aliphatic acids, anhydrides, ethers and water, therefore, *N,N*-dialkylamides stabilize t_{2g} orbitals and unstabilize e_g orbitals in octahedral transition-metal complexes. This suggests that Cr^{2+} ($(t_{2g})^3(e_g)^1$ electron configuration) and Co^{2+} ($(t_{2g})^5(e_g)^2$) ions are labilized by *N,N*-dialkylamides ligands, while on the contrary, Cr^{3+} ($(t_{2g})^3(e_g)^0$) and Co^{3+} ($(t_{2g})^6(e_g)^0$) are stabilized by them; *i.e.*, the reducing power of both Cr^{2+} and Co^{2+} ions is increased by the coordination of *N,N*-dialkylamides. Accordingly, it may be concluded that, in the presence of *N,N*-dialkylamides, Reaction 3 proceeds relatively smoothly and that α-tetralone is produced in a very high yield.

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