Liquid-phase Oxidation of Hydrocarbons with Molecular Oxygen. I. The Effects of Metal Ions and Their Ligands on Product Distribution in the Oxidation of Tetralin in Acetic Acid

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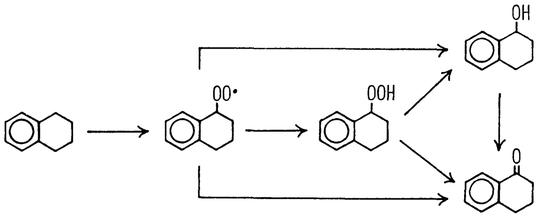
Metal-ion catalyzed oxidation of tetralin and metal-ion catalyzed decomposition of α-tetralin hydroperoxide (THP) were carried out in acetic acid in both the presence and absence of an additive. It was found that the rate-determining step in the oxidation of tetralin is the decomposition of THP. The results also suggest that the decomposition of THP with cobalt catalysts proceeds by the inner-sphere mechanism. In the oxidation of tetralin catalyzed by first-transition-metal ions, excepting vanadium, cobalt showed the highest activity and the lowest selectivity of hydroperoxide, and chromium showed the highest ratio of α-tetralone to α-tetralol (On/Ol). The order of the activities of metal acetates in producing oxidation is in agreement with that of the activities of metal acetates in producing decomposition. Such agreement was also found for $Co(acac)_3$, $Cr(acac)_3$, $Mn(acac)_2$, and $Fe(acac)_3$ catalysts. For oxidation with $Co(OAc)_2 \cdot 4H_2O$ and $Cr(OAc)_3$, the product distributions were examined for various conversions of tetralin. In the both cases, the On/Ol ratios increase with increasing tetralin conversion. However, the mechanisms responsible for the increase in the On/Ol ratio appear to be different.

Liquid-phase oxidation of tetralin has been widely studied in both the presence and absence of a catalyst. The main products are known to be α-tetralin hydroperoxide (THP), α-tetralone and α-tetralol. According to previous studies,[1–10] the formation mechanism is understood as follows:



However, previous reports dealt mainly with kinetics and thus with reactions at low conversion in order to avoid complications. There are few data in the literature on the distribution of the products at high conversion.[6]

It is well known that transition-metal ions catalyze the oxidation of hydrocarbons and their catalytic activities are frequently related to their redox potentials.[11,12] It is also clear that metal ions in solution form complexes with solvent molecules, counter anions, *etc.*, and that the redox potentials of these ions are affected by ligands in the complex. However, there are not many reports dealing with the influence of ligands on the distribution of the products for metal-ion catalyzed autoxidation of aromatic hydrocarbons.

The aim of the present study is to elucidate the effects of various metal ions and their ligands on the oxidation of tetralin, in addition to the dependence of the product distribution on the catalyst and the substrate concentration at various reaction temperatures.

Experimental

Materials. The tetralin and metal salts employed were of reagent grade and were used without further purification. THP was synthesized according to the procedure of Knight and Swern.[13] This hydroperoxide was 99.8% pure as confirmed by iodometric titration.

Oxidation of Tetralin. A mixture (150 cm^3) of tetralin and acetic acid containing a catalyst was placed into an autoclave (sus-316) equipped with a magnetic stirrer and a thermocouple, and was warmed to the desired temperature. Oxygen was introduced into the autoclave through a pressure controller (the oxygen pressure was 20 kg/cm^2). The reaction temperature was controlled to within ±1.0 °C of the desired temperature by occasional cooling with water.

The reaction 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 acetic acid 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 acetic acid containing 2.50 g of THP and then the nitrogen stream was stopped. At hourly intervals, 1.5-cm^3 portions of the reaction mixture were withdrawn in a nitrogen atmosphere and were analyzed.

Analysis. The hydroperoxide concentration was determined by the usual method.[14]

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 170°, He 40 cm^3/min). *o*-Bromoanisole was used as an 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 hydroperoxide before reduction.

Results and Discussion

The dissolving rate for molecular oxygen in a solution is frequently the rate-determining step in the liqid-phase autoxidation of hydrocarbons at atmospheric pressure. In the present study, the oxidation rate of tetralin in acetic acid was actually faster at higher pressure than at atmospheric pressure, and was nearly constant at oxygen pressures greater than 4 kg/cm^2. All runs in

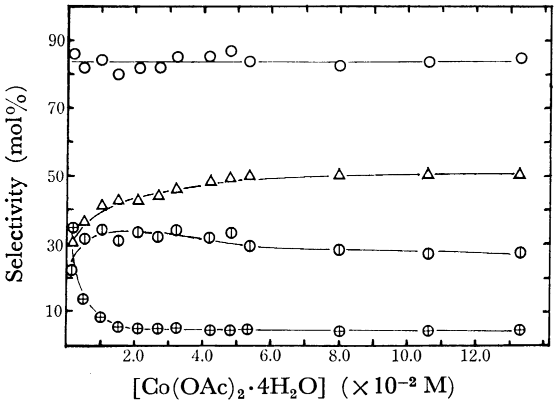


Fig. 1. The effect of cobalt acetate concentration on the oxidation of tetralin in acetic acid at 72.5±1.0 °C.
Reaction conditions: [tetralin]$_{\text{initial}}$=3.85 M; O$_2$ pressure, 20 kg/cm^2; tetralin conversion, 20.0±1.5%.
△: Tetralone, ⦶: tetralol, ⊕: peroxide, ○: total.

the present study were, therefore, carried out at an oxygen pressure of 20 kg/cm^2.

The Effects of the Cobalt and Tetralin Concentrations and the Reaction Temperature. The effect of the Co(OAc)$_2$·4H$_2$O concentration on the formation of products in the oxidation of tetralin in acetic acid at 72.5 °C is shown in Fig. 1. The dependence of the product distribution on the initial concentration of tetralin is shown in Fig. 2. Figure 3 shows the selectivities* of products at various reaction temperatures in the range from 50 to 110 °C. At reaction temperatures greater than 130 °C, hydroperoxide, α-tetralol and α-tetralone were obtained with lower selectivities than at reaction temperatures below 110 °C. At reaction temperatures above 120 °C, it was also difficult to carry out the oxidation of tetralin at an approximately constant temperature.

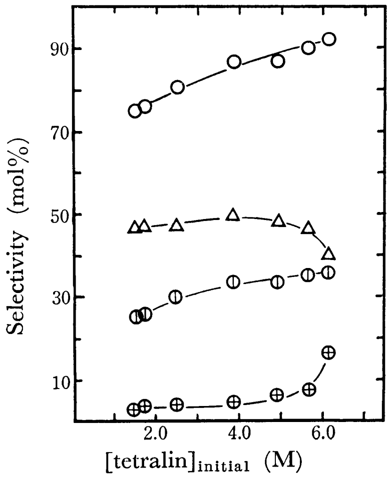


Fig. 2. The cobalt acetate catalyzed oxidation of tetralin in acetic acid at 72.5±1.0 °C.
Reaction conditions: [Co(OAc)$_2$·4H$_2$O]=4.77×10^{-2} M; O$_2$ pressure, 20 kg/cm^2; tetralin conversion, 20.0±2.0%.
△: Tetralone, ⦶: tetralol, ⊕: peroxide, ○: total.

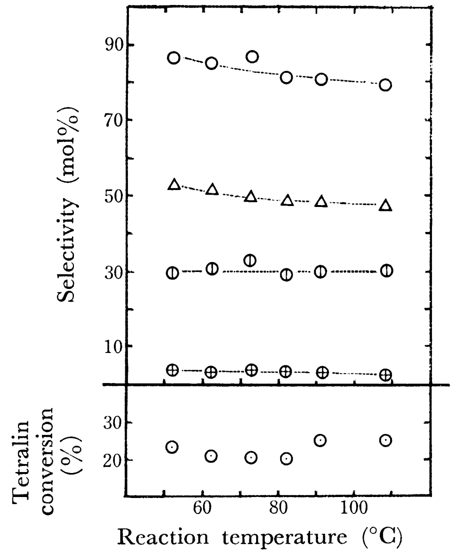
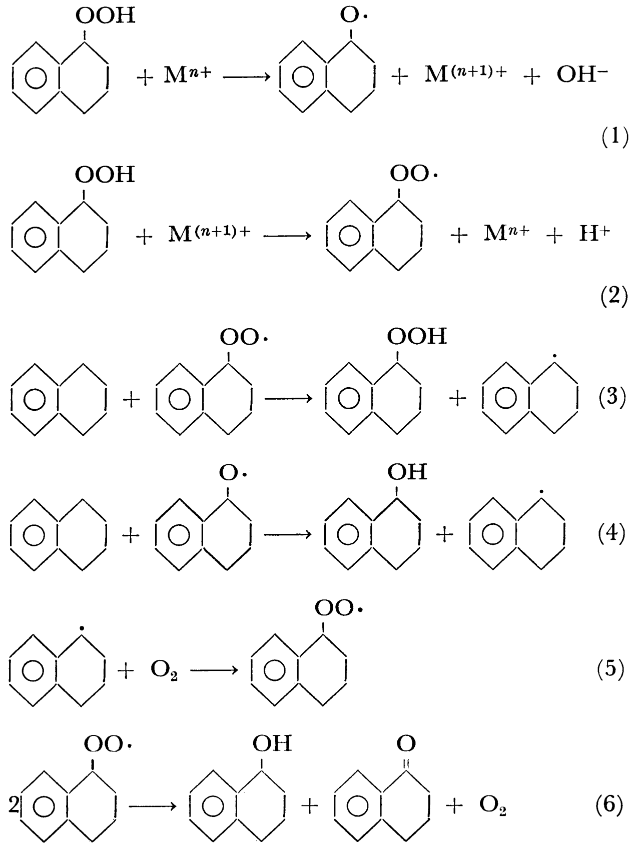


Fig. 3. The effect of reaction temperature on the oxidation of tetralin in acetic acid.
Reaction conditions: [Co(OAc)$_2$·4H$_2$O]=4.77×10^{-2} M; [tetralin]$_{\text{initial}}$=3.85 M; O$_2$ pressure, 20 kg/cm^2.
△: Tetralone, ⦶: tetralol, ⊕: peroxide, ○: total.

The selectivity of hydroperoxide formation decreases rapidly with increasing Co(OAc)$_2$·4H$_2$O concentration (Fig. 1) and upon decreasing the initial tetralin concentration (Fig. 2). This result can be explained by the following reaction scheme which has been proposed



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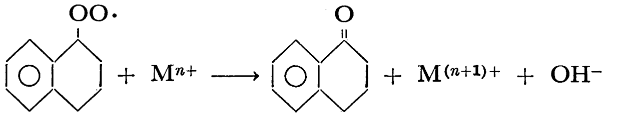
* In this paper, the term "selectivity" means the molar percentage of the product to the amount of the converted tetralin.



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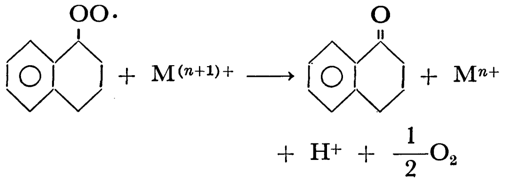

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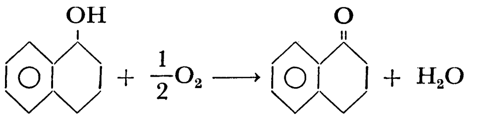

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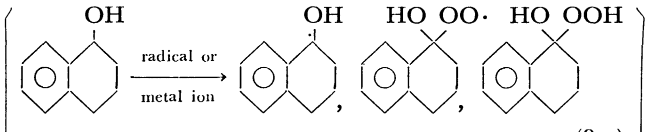

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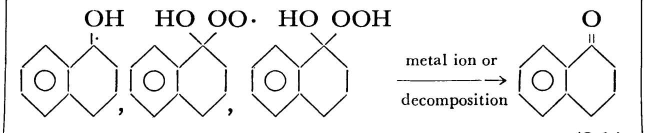


(9-b)

by other workers.[1—10,16,17] Transition-metal ions generally promote the decomposition of hydroperoxide following Reactions 1 and 2. Accordingly, the selectivity of hydroperoxide decreases with increasing $Co(OAc)_2 \cdot 4H_2O$ concentration.

Figures 4 and 5 show the product formation for various tetralin conversions. The product distributions shown in Fig. 4 are similar in tendency to those shown in Fig. 5, although the catalyst concentration depicted in Fig. 4 is different from that in Fig. 5. The α-tetralone selectivity increases with increasing tetralin conversion. For tetralin conversions above 20%, the percentage of the decrease in α-tetralol selectivity is nearly equal to that of the increase in α-tetralone selectivity (Fig. 4). Martan *et al.*[6] have stated that, in the $Co(OAc)_2$-catalyzed co-oxidation of tetralin and α-tetralol in acetic acid at 80 °C, α-tetralol is oxidized at a rate 1.5 times faster than tetralin and gives α-tetralone in a 75% yield. Accordingly, the increase in α-tetralone selectivity for tetralin conversions above 20% appears to be mainly due to Reaction 9.

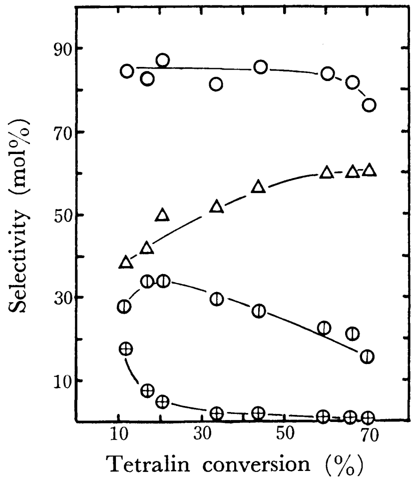


Fig. 4. The cobalt acetate catalyzed oxidation of tetralin in acetic acid at 72.5±1.0 °C.
Reaction conditions: $[Co(OAc)_2 \cdot 4H_2O] = 4.77 \times 10^{-2}$ M; $[\text{tetralin}]_{\text{initial}} = 3.85$ M; O_2 pressure, 20 kg/cm^2.
△: Tetralone, ⦶: tetralol, ⊕: peroxide, ○: total.

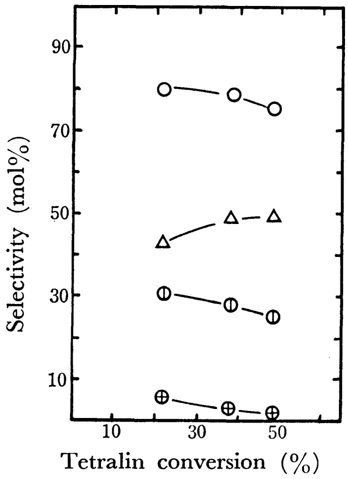


Fig. 5. The cobalt acetate catalyzed oxidation of tetralin in acetic acid at 72.0±2.0 °C.
Reaction conditions: $[Co(OAc)_2 \cdot 4H_2O] = 1.46 \times 10^{-2}$ M; $[\text{tetralin}]_{\text{initial}} = 3.50$ M; O_2 pressure, 20 kg/cm^2.
△: Tetralone, ⦶: tetralol, ⊕: peroxide, ○: total.

From Figs. 1—5, when cobalt(II) acetate is used as a catalyst and acetic acid as a solvent, the optimum conditions for obtaining α-tetralone are concluded to be as follows: a reaction temperature below 80 °C, an initial concentration of tetralin from 2.5 to 5 M, a catalyst concentration above 4.5×10^{-2} M and a tetralin conversion above 50%.

The Effect of Ligands. The effects of various counter anions and additives on the oxidation of tetralin catalyzed by cobalt ions are shown in Tables 1—4 and Fig. 6. It is clear that the additives used coordinate to the cobalt ion in a solution of acetic acid because the color of the solution containing cobalt acetate changes upon introduction of the additive.

As shown in Tables 1 and 3 and in Fig. 6, it is clear that cobalt(II) dibromide has a low catalytic activity although the rate of cobalt-catalyzed oxidation of tetralin is accelerated by adding potassium bromide to cobalt(II) acetate solutions (Co : KBr = 1 : 1, molar ratio). This has already been observed and demonstrated kinetically.[7,10]

The tris(acetylacetonate)cobalt(III) complex ($Co(acac)_3$) showed a higher selectivity for hydroperoxide formation and a slower rate of oxidation than catalysts such as cobalt(II) carboxylates, cobalt(II) nitrate and bis(acetylacetonato)cobalt(II) complexes ($Co(acac)_2$ and $Co(acac)_2 \cdot 2H_2O$) (Tables 1 and 2, and Fig. 6). The addition of KF, pyridine (py) and 2,2′-bipyridine (bipy) to the $Co(OAc)_2 \cdot 4H_2O$ solution (Co-F, Co-py and Co-bipy) decreased the tetralin oxidation rate and increased the hydroperoxide selectivity (Tables 3 and 4, and Fig. 6). Thus, when hydroperoxide was ob-

TABLE 1. PRODUCT DISTRIBUTION FOR THE COBALT SALT CATALYZED OXIDATION OF TETRALIN

Catalyst	Tetralin conversion (%)	Selectivity (mol%) Tetralone	Tetralol	Peroxide	Total	Reaction temperature (°C)
$Co^{II}(OAc)_2\cdot 4H_2O$	20.9	49.1	32.3	4.8	86.2	72.5±0.5
$Co^{II}(C_6H_5CO_2)_2$	18.7	49.0	34.5	3.7	87.2	72.5±1.0
$Co^{II}(C_{18}H_{35}O_2)_2$	20.4	53.1	33.1	3.9	90.1	72.5±1.0
$Co^{II}(NO_3)_2\cdot 6H_2O$	19.2	44.7	31.7	7.8	84.2	71.5±1.0
$Co^{III}(acac)_3$	19.9	41.9	29.0	18.4	89.3	72.5±1.0
$Co^{II}Br_2\cdot 6H_2O$ a)	38.6	27.3	19.1	2.5	48.9	130—170

Reaction conditions : [catalyst] = 4.77×10^{-2} M, $[\text{tetralin}]_{\text{initial}}$ = 3.85 M, the O_2 pressure was 20 kg/cm^2.

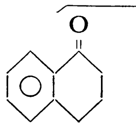
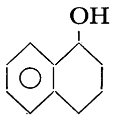
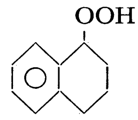
a) No oxygen absorption was observed for a period of 2 h at 72.5 °C.

TABLE 2. PRODUCT DISTRIBUTION FOR THE ACETYLACETONATO COBALT COMPLEX CATALYZED OXIDATION OF TETRALIN

Catalyst	Tetralin conversion (%)	Selectivity (mol%) Tetralone	Tetralol	Peroxide	Total	Reaction time (min)
$Co^{II}(OAc)_2\cdot 4H_2O$	22.3	53.2	30.3	4.3	87.8	40
$Co^{III}(acac)_3$	20.2	39.7	25.1	26.6	91.4	66
$Co^{II}(acac)_2$	19.0	46.9	30.9	6.0	83.8	37
$Co^{II}(acac)_2\cdot 2H_2O$	17.6	48.9	32.1	5.3	86.3	35

Reaction conditions : [catalyst] = 4.77×10^{-2} M, $[\text{tetralin}]_{\text{initial}}$ = 3.85 M, the reaction temperature was 50.0±1.0 °C, the O_2 pressure was 20 kg/cm^2.

TABLE 3. PRODUCT DISTRIBUTION FOR THE COBALT ACETATE CATALYZED OXIDATION OF TETRALIN IN THE PRESENCE OF ADDITIVE

Additive	Tetralin conversion (%)	Selectivity (mol%) 			Total	Reaction time (min)
—	22.3	53.2	30.3	4.3	87.8	40
KCl	22.5	48.7	33.9	4.1	86.7	50
KBr	21.3	52.7	31.1	5.5	89.3	24
KSCN a)	21.7	47.3	28.5	6.8	82.6	39
Pyridine	21.1	47.2	30.3	11.4	88.9	50
KF	23.3	43.8	28.8	15.2	87.8	64

Reaction conditions : $[Co(OAc)_2\cdot 4H_2O]$ = [additive] = 4.77×10^{-2} M, $[\text{tetralin}]_{\text{initial}}$ = 3.85 M, the reaction temperature was 50.0±1.0 °C, the O_2 pressure was 20 kg/cm^2.

a) A brown material was deposited during the oxidation reaction.

TABLE 4. PRODUCT DISTRIBUTION FOR THE COBALT ACETATE CATALYZED OXIDATION OF TETRALIN IN THE PRESENCE OF BIPYRIDINE

Catalyst (M) $Co(OAc)_2\cdot 4H_2O$	Bipyridine	Tetralin conversion (%)	Selectivity (mol%) Tetralone	Tetralol	Peroxide	Total	Reaction temperature (°C)	Reaction time (min)
0.0052	0.0052	19.4	28.8	27.1	31.0	86.9	72.5±1.0	12
0.0105	0.0105	21.4	36.1	32.1	24.4	92.6	72.5±1.0	10
0.0159	0.0159	19.2	35.7	33.0	17.7	86.4	72.5±1.0	9
0.0213	0.0213	19.6	35.5	33.2	14.8	83.5	74.0±1.5	8
0.0266	0.0266	20.2	38.2	31.4	13.8	83.4	72.5±1.0	9
0.0051	0.0103	16.4	11.3	1.5	63.9	76.7	72.0±0.5	55
0.0104	0.0207	18.4	10.3	1.5	52.1	63.9	72.0±0.5	50
0.0107	—	20.9	40.6	34.7	8.0	83.3	64—70	12

Reaction conditions : $[\text{tetralin}]_{\text{initial}}$ = 3.85 M, the O_2 pressure was 20 kg/cm^2.

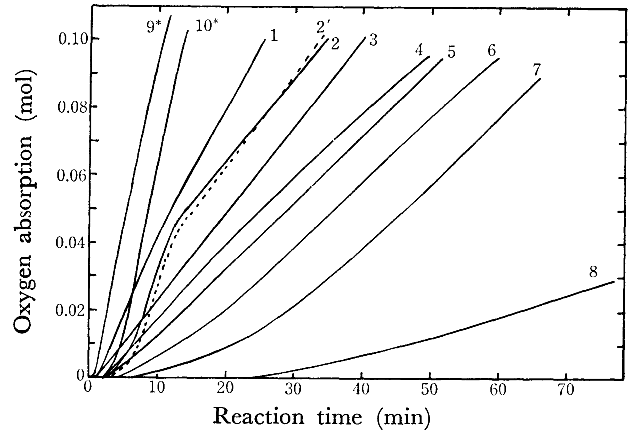


Fig. 6. The oxidation of tetralin in acetic acid at 50.0±1.0 °C.
Reaction conditions: [metal ion or complex] = [additive] = 4.77×10^{-2} M; $[\text{tetralin}]_{\text{initial}}=3.85$ M; O_2 pressure, 20 kg/cm².
1: $Co^{II}(OAc)_2\cdot4H_2O+KBr$ (Co-Br), 2: $Co^{II}(acac)_2\cdot2H_2O$, 2': $Co^{II}(acac)_2$, 3: $Co^{II}(OAc)_2\cdot4H_2O$, 4: $Co^{II}(OAc)_2\cdot4H_2O+KCl$ (Co-Cl), 5: $Co^{II}(OAc)_2\cdot4H_2O$+pyridine (Co-py), 6: $Co^{II}(OAc)_2\cdot4H_2O+KF$ (Co-F), 7: $Co^{III}(acac)_3$, 8: $Mn^{II}(OAc)_2\cdot4H_2O$, 9*: $Co^{II}(OAc)_2\cdot4H_2O$, 10*: $Co^{III}(acac)_3$.
*) The reaction temperature is 72.5±1.0 °C.

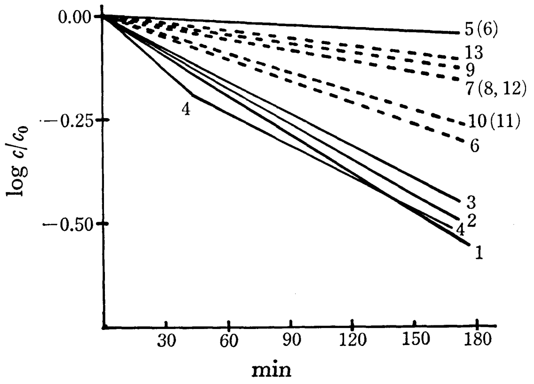


Fig. 7. The decomposition of THP in acetic acid.
——: Reaction temperature, 51.0±1.0 °C; $[\text{THP}]_{\text{initial}}=2.00\times10^{-1}$ M; [metal ion or complex] = [additive] = 2.0×10^{-3} M.
----: Reaction temperature, 72.0±1.0 °C; $[\text{THP}]_{\text{initial}}=2.00\times10^{-1}$ M; [metal ion or complex] = 6.0×10^{-3} M.
1: $Co^{II}(OAc)_2\cdot4H_2O$, 2: $Co^{II}(OAc)_2\cdot4H_2O$+pyridine (Co-py), 3: $Co^{II}(OAc)_2\cdot4H_2O+KF$ (Co-F), 4: $Co^{II}(acac)_2$, 5: $Co^{III}(acac)_3$, 6: $Mn^{II}(OAc)_2\cdot4H_2O$, 7: $Cr^{III}(OAc)_3$, 8: $Ni^{II}(OAc)_2\cdot4H_2O$, 9: $Cu^{II}(OAc)_2\cdot H_2O$, 10: $Cr^{III}(acac)_3$, 11: $Mn^{II}(acac)_2$, 12: $Ti^{IV}O(acac)_2$, 13: $Fe^{III}(acac)_3$.

tained in high selectivities, the oxidation rate of tetralin was low.

The decomposition of THP with five kinds of cobalt catalysts was also carried out in acetic acid at 51 °C in a nitrogen atmosphere. This was carried out at lower catalyst concentrations than those for the oxidation of tetralin, because the decomposition was too fast at high catalyst ($[Co(OAc)_2\cdot4H_2O]>6.0\times10^{-3}$ M) concentrations. The decomposition rates were first order with respect to the hydroperoxide concentration. The decomposition order is $Co(acac)_2\simeq Co(OAc)_2\cdot4H_2O>$ Co-py $>$ Co-F $\gg Co(acac)_3$, as shown in Table 5 and Fig. 7. This order is consistent with that of the oxidation rates of tetralin at 50°, that is, $Co(acac)_2\simeq Co(OAc)_2\cdot4H_2O>$ Co-py $>$ Co-F $\gg Co(acac)_3$ (Tables 2 and 3, and Fig. 6) and also corresponds to the order of increasing hydroperoxide selectivities for oxidation ($Co(OAc)_2\cdot4H_2O\simeq Co(acac)_2<$ Co-py $<$ Co-F $\ll Co(acac)_3$) (Tables 2 and 3, and Fig. 6). Yamada and Kamiya[18] have reported that the rate of $Co(OAc)_2$-catalyzed decomposition of THP in acetic acid at 50 °C lowers as the molar ratio of the bipy added to the cobalt(II) acetate is increased from zero to two. For the $Co(OAc)_2\cdot4H_2O$-catalyzed oxidation of tetralin in acetic acid at

Table 5. Rate constants for the decomposition of THP in acetic acid

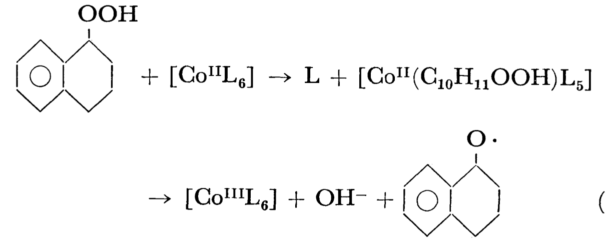
Catalyst		Reaction temperature (°C)	Rate constant ($\times10^{-3}$ min^{-1})
Metal salt or metal complex	Concentration (M)		
$Co^{II}(OAc)_2\cdot4H_2O$	2.0×10^{-3}	51.0±1.0	7.5
Co-py[a]	2.0×10^{-3}	51.0±1.0	6.6
Co-F[b]	2.0×10^{-3}	51.0±1.0	5.8
$Co^{II}(acac)_2$	2.0×10^{-3}	51.0±1.0	10.0 6.2
$Co^{III}(acac)_3$	2.0×10^{-3}	51.0±1.0	0.7
$Mn^{II}(OAc)_2\cdot4H_2O$	2.0×10^{-3}	51.0±1.0	0.6
	6.0×10^{-3}	72.0±1.0	3.9
$Cr^{III}(OAc)_3$	6.0×10^{-3}	72.0±1.0	2.0
$Ni^{II}(OAc)_2\cdot4H_2O$	6.0×10^{-3}	72.0±1.0	1.9
$Cu^{II}(OAc)_2\cdot H_2O$	6.0×10^{-3}	72.0±1.0	1.7
$Cr^{III}(acac)_3$	6.0×10^{-3}	72.0±1.0	3.4
$Mn^{II}(acac)_2$	6.0×10^{-3}	72.0±1.0	3.3
$Ti^{IV}O(acac)_2$	6.0×10^{-3}	72.0±1.0	2.0
$Fe^{III}(acac)_3$	6.0×10^{-3}	72.0±1.0	1.5

a) $Co^{II}(OAc)_2\cdot4H_2O$: pyridine = 1 : 1 (molar ratio). b) $Co^{II}(OAc)_2\cdot4H_2O$: KF = 1 : 1 (molar ratio). $[\text{THP}]_{\text{initial}}=2.00\times10^{-1}$ M.

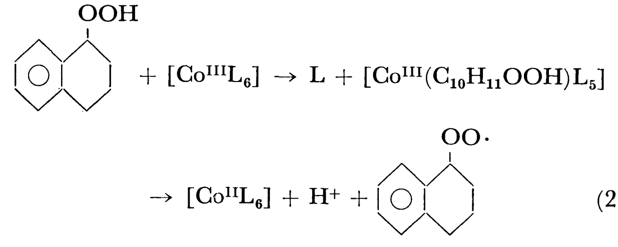
72.5 °C, the hydroperoxide selectivity increases as the ratio of the bipy to the cobalt(II) acetate is increased from zero to two (Table 4). Accordingly, the tetralin oxidation rate and the selectivity for the formation of hydroperoxide, for such cobalt catalysts, depend on the hydroperoxide decomposition rate.

From the above results, the decomposition mechanism of hydroperoxide can also be considered to be as follows. The catalytic decomposition of hydroperoxide by metal ions is thought to proceed *via* the formation of inner-sphere and/or outer-sphere complexes of metal ions with hydroperoxide[19] (inner-sphere[20–23] and/or outer-sphere mechanisms[20–23]). For the inner-sphere mechanism, the ligand attached to the metal ion must be replaced by the hydroperoxide, *i.e.*, $[ML_5Y]+ROOH \rightarrow [ML_5(ROOH)]+Y$. Such replacement is not required for the formation of the outer-sphere complex. Accordingly, decomposition by the outer-sphere mechanism will depend mainly on the redox potential of the complex. On the other hand, decomposition by the inner-sphere mechanism appears to depend on the mobility of the ligands attached to the metal ion, as well as on the redox potential of the metal ion.

The following facts are well known in coordination chemistry. Ligands such as py and F^- form strong coordination bonds with cobalt ions in comparison with ligands such as NO_3^-, Br^-, Cl^-, H_2O, and RCO_2^-.[20–24] For hydrolysis of the type, $[ML_5Y]+H_2O \rightarrow [ML_5(H_2O)]+Y$ ($M=Co^{III}$ or Cr^{III}, $L=NH_3$ or H_2O), the order of reactivities as far as the leaving group (Y) is concerned is $NO_3^- > Br^- > H_2O > AcO^- > F^- > NH_3$.[20,23,25] This is in good agreement with the order of stability constants of $[ML_5Y]$.[20,23] The cobalt complex having the $(t_{2g})^5(e_g)^2$ electron configuration ($Co^{II}(acac)_2L_2$, $L=H_2O$ or AcOH) has a faster rate for the ligand-replacement reaction than the corresponding cobalt complex having the $(t_{2g})^6(e_g)^0$ electron configuration ($Co^{III}(acac)_2L_2$, $L=H_2O$ or AcOH, $L_2=$ acac).[20,23,25] In solution, $Co^{II}(acac)_2$ forms $Co^{II}(acac)_2L_2$ with solvent molecules such as AcOH and H_2O, although $Co^{II}(acac)_2$ has a tetrameric structure in the solid state.[22] 2,2′-Bipyridine coordinated to transition-metal ions generally can be replaced by other ligands only with difficulty.[20–24] Therefore, the fact that catalysts such as $Co(acac)_3$, Co-F, Co-py, and Co-bipy have high hydroperoxide selectivities for the oxidation of tetralin and low rates for the decomposition of THP is mainly correlated with the stability of the ligands attached to the cobalt ion if Reaction 1 and/or Reaction 2 proceed by the inner-sphere mechanism as follows:



(1′)



(2′)

L : RCO_2^-, Br^-, Cl^-, F^-, OH^-, AcOH, H_2O, py,
L_2 : $acac^-$, bipy.

However, the possibility cannot be completely excluded that the high hydroperoxide selectivity and the low tetralin oxidation rate in the case of Co-py and Co-bipy are attributable to retarding effects of py and bipy on the autoxidation of hydrocarbons.[26,27]

When the bis(acetylacetonato)cobalt(II) complex is used as a catalyst, the oxygen absorption curve for the oxidation of tetralin has an irregular bending point (Fig. 6) and the decomposition of THP has two rate constants (Fig. 7 and Table 5). On the other hand, $Co(acac)_3$ shows neither such a bending point in the oxidation curve nor two decomposition rate constants. These results are interpreted as follows. Acetylacetonate in $Co(acac)_2L_2$ appears to be easily oxidized compared with that in $Co(acac)_3$ because $Co(acac)_2L_2$ is relatively labile. On the contrary, acetylacetonate in $Co(acac)_3$ is relatively difficult to oxidize because of the stability of $Co(acac)_3$. The redox potential and the rate of ligand replacement are also different from those for $Co(acac)_2L_2$ and the complex containing the new ligands which result from the oxidation of acetylacetonate. Therefore, the bis(acetylacetonato)-cobalt(II) complex is thought to show an irregular bending point in the oxidation and two decomposition rate constants.

The Effect of Metal Ions. The effects of various

TABLE 6. PRODUCT DISTRIBUTION FOR THE METAL ACETATE CATALYZED OXIDATION OF TETRALIN

Catalyst	Tetralin conversion (%)	Selectivity (mol%)				Molar ratio tetralone/tetralol	Reaction time (min)
		Tetralone	Tetralol	Peroxide	Total		
$Cr^{III}(OAc)_3$[a]	18.9	32.6	2.7	55.0	90.3	12.10	59
$Mn^{II}(OAc)_2 \cdot 4H_2O$	22.2	21.2	10.8	54.3	86.3	1.97	49
$Co^{II}(OAc)_2 \cdot 4H_2O$	20.9	49.1	32.3	4.8	86.2	1.52	7
$Ni^{II}(OAc)_2 \cdot 4H_2O$	20.5	18.0	8.4	68.0	94.4	2.15	53
$Cu^{II}(OAc)_2 \cdot H_2O$	18.8	16.3	8.9	59.9	85.1	1.83	285

Reaction conditions : [metal acetate] $= 4.77 \times 10^{-2}$ M, $[tetralin]_{initial} = 3.85$ M, the reaction temperature was 72.5± 1.0 °C, the O_2 pressure was 20 kg/cm².

a) A small part of the amount added remained undissolved.

Table 7. Product distribution for the acetylacetonato complex catalyzed oxidation of tetralin

Catalyst	Tetralin conversion (%)	Selectivity (mol%)				Molar ratio tetralone/tetralol	Reaction time (min)
		Tetralone	Tetralol	Peroxide	Total		
$Ti^{IV}O(acac)_2$[a]	17.6	17.5	15.1	33.4	66.0	1.16	300
$Cr^{III}(acac)_3$	20.3	30.9	9.4	50.1	90.4	3.30	64
$Mn^{II}(acac)_2$	20.6	21.3	11.9	52.3	85.5	1.79	70
$Fe^{III}(acac)_3$[a]	19.6	12.8	4.2	72.6	89.6	3.08	150
$Co^{III}(acac)_3$	19.9	41.9	29.0	18.4	89.3	1.44	12

Reaction conditions : [acetylacetonato complex] $= 4.77\times10^{-2}$ M, $[\text{tetralin}]_{\text{initial}} = 3.85$ M, the reaction temperature was 72.5±1.0 °C, the O_2 pressure was 20 kg/cm^2.

a) A small part of the amount added remained undissolved.

metal acetates and acetylacetonato complexes on the oxidation of tetralin in acetic acid at 72.5 °C are shown in Figs. 8—10 and Tables 6 and 7. The decomposition of THP with various metal acetates and acetylacetonato complexes was also carried out in acetic acid at 72.0 °C in a nitrogen atmosphere (Fig. 7 and Table 5).

In the oxidation of tetralin catalyzed by five kinds of metal acetates, the hydroperoxide selectivities increase in the order $Co \ll Mn \simeq Cr < Cu < Ni$ and the activity order of these catalysts is $Co \gg Mn \simeq Cr \simeq Ni > Cu$ (Table 6 and Fig. 8). This is in agreement with the order of activities for the decomposition of THP by these catalysts (Fig. 7 and Table 5). Therefore, the orders of the hydroperoxide selectivities and the oxidations rate are thought to arise from the differences in the decomposition rates of hydroperoxide produced in the oxidation of tetralin. The differences between the decomposition rates also appear to be mainly attributable to differences between the redox potentials of the five metal acetates in acetic acid because the activity order of these five metal acetates for the decomposition of THP is not consistent with the reactivity sequence predicted on the basis of crystal field theory[20,23] for the ligand-replacement reactions of the five metal acetato complexes. The fact that $Cu(OAc)_2\cdot H_2O$ exhibits a lower hydroperoxide selectivity than $Ni(OAc)_2\cdot 4H_2O$ appears to involve the prolonged oxidation time of $Cu(OAc)_2\cdot H_2O$. The extent of thermal decomposition appears to become gradually greater with increasing reaction time. As a second reason, it is thought that the concentration of monomeric $Cu(OAc)_2\cdot H_2O$ increases during the prolonged reaction time. It has been reported that $Cu(OAc)_2\cdot H_2O$ is dimeric in many nonaqueous solvents[28,29] and partially dissociates into its monomeric form in acetic acid.[30] Imamura *et al.*[31] have also found that in the $Cu(OAc)_2\cdot H_2O$-catalyzed decomposition of THP in acetic acid at 80 °C, the addition of LiCl to the solution increases the concentration of monomeric copper(II) acetate and accelerates the decomposition of THP.

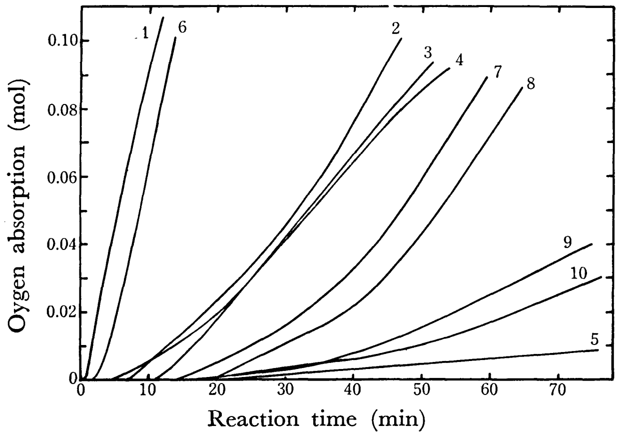


Fig. 8. The oxidation of tetralin in acetic acid at 72.5±1.0 °C.

Reaction conditions: [metal ion or complex] $= 4.77\times10^{-2}$ M; $[\text{tetralin}]_{\text{initial}} = 3.85$ M; O_2 pressure, 20 kg/cm^2.

1: $Co^{II}(OAc)_2\cdot 4H_2O$, 2: $Mn^{II}(OAc)_2\cdot 4H_2O$, 3: $Ni^{II}(OAc)_2\cdot 4H_2O$, 4: $Cr^{III}(OAc)_3$, 5: $Cu^{II}(OAc)_2\cdot H_2O$, 6: $Co^{III}(acac)_3$, 7: $Cr^{III}(acac)_3$, 8: $Mn^{II}(acac)_2$, 9: $Ti^{IV}O(acac)_2$, 10: $Fe^{III}(acac)_3$.

Agreement between the oxidation of tetralin and the decomposition of THP is also found for four acetylacetonato complexes, excepting $TiO(acac)_2$, as well as, for the five kinds of metal acetate catalysts. Specifically, the catalyst which exhibits a high hydroperoxide selectivity and a slow oxidation rate has a relatively low decomposition rate, *i.e.*, the orders of activities for oxidation, as well as for decomposition, are $Co \gg Cr \simeq Mn > Fe$ (Tables 5 and 7, and Fig. 7). This order appears to arise mainly from the differences in the redox potentials of the four acetylacetonato complexes in acetic acid because this order is inconsistent with the reactivity sequence expected on the basis of the stability constants[23,32,33] of acetylacetonato complexes for the ligand-replacement reaction. $TiO(acac)_2$, which has a d^0 system, is abnormal with respect to the acetylacetonato complexes used in the present work. This result cannot be interpreted explicitly at present.

As shown in Tables 6 and 7, the ratio of α-tetralone to α-tetralol (On/Ol) obtained for oxidation with a chromium catalyst is relatively high. The product distributions for oxidation with $Cr(OAc)_3$ were examined at various tetralin conversion. The selectivity of α-tetralone rises and that of hydroperoxide decreases as the conversion of tetralin increases for oxidation (Figs. 9 and 10). The degree of the increase in the α-tetralone selectivity is nearly equal to that of the decrease in the hydroperoxide selectivity. For $Cr(OAc)_3$-catalyzed decomposition of THP in acetic acid at 72.0 °C in a nitrogen atmosphere, α-tetralone and α-acetoxytetralin were obtained in about 70 and 10% selectivities, respectively, at 10—25% THP conversions.

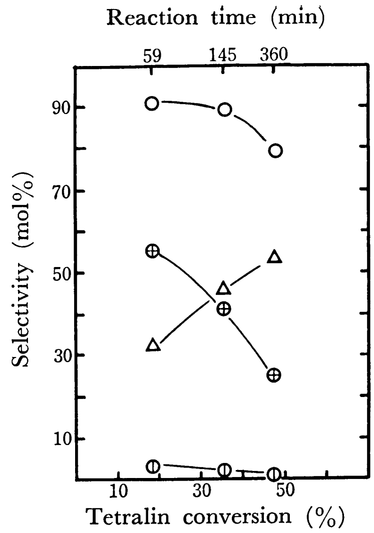


Fig. 9. The chromium(III) acetate catalyzed oxidation of tetralin in acetic acid at 72.5±1.0 °C.
Reaction conditions: $[Cr(OAc)_3]=4.77\times10^{-2}$ M; $[\text{tetralin}]_{\text{initial}}=3.85$ M; O_2 pressure, 20 kg/cm^2.
△: Tetralone, ⦶: tetralol, ⊕: peroxide, ○: total.

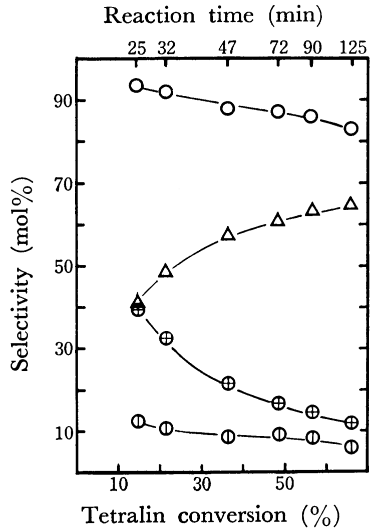
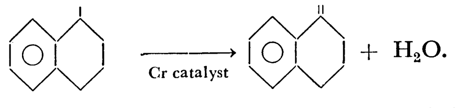


Fig. 10. The Cr–Co catalyzed oxidation of tetralin in acetic acid at 72.5±1.0 °C.
Reaction conditions: $[Cr(OAc)_3]=4.77\times10^{-2}$ M; $[Co(OAc)_2\cdot4H_2O=0.13\times10^{-2}$ M; $[\text{tetralin}]_{\text{initial}}=3.85$ M; O_2 pressure, 20 kg/cm^2.
△: Tetralone, ⦶: tetralol, ⊕: peroxide, ○: total.

α-Tetralol was produced only in small amounts. Therefore, it is thought that for $Cr(OAc)_3$-catalyzed oxidation, the main pathway which contributes to the increase of α-tetralone is not Reaction 9 but the THP dehydration reaction:



This dehydration reaction can be resolved into Reactions 2 (Cr^{3+} consumption) and 7 (Cr^{3+} regeneration) as far as the variable valence of the chromium ion is concerned. If hydroperoxide is dehydrated by a process in which the chromium valence remains unchanged, the formation of α-tetralone will be related to the hydration energy of the chromium ion. However, this is not the usual process for the decomposition of hydroperoxide catalyzed by a transition-metal ion. In addition, the increasing order of the On/Ol ratios for the metal-catalyzed oxidation of tetralin (Tables 6 and 7) is inconsistent with the order of hydration heats[20,23] of the first-transition-metal ions.

For the purposes of obtaining α-tetralone in higher yields, binary metal ions (Cr and Co) were used as a catalyst for the oxidation of tetralin (Fig. 10). However, the binary catalyst showed only a slight increase in the α-tetralone selectivity compared with the $Co(OAc)_2\cdot4H_2O$ catalyst (Figs. 4 and 10).

References

1) A. Robertson and W. A. Waters, *J. Chem. Soc.*, **1948**, 1574.

2) A. E. Woodward and R. B. Mesrobian, *J. Am. Chem. Soc.*, **75**, 6189 (1953).

3) Y. Kamiya, S. Beaton, A. Lafortune, and K. U. Ingold, *Can. J. Chem.*, **41**, 2020 (1963).

4) Y. Kamiya and K. U. Ingold, *Can. J. Chem.*, **42**, 2424 (1964).

5) A. Mukherjee and W. F. Graydon, *J. Phys. Chem.*, **71**, 4232 (1967).

6) M. Martan, J. Manassen, and D. Vofsi, *Tetrahedron*, **26**, 3815 (1970).

7) A. S. Hay and H. S. Blanchard, *Can. J. Chem.*, **43**, 1306 (1965).

8) A. I. Kamneva, V. I. Zakharova, L. N. Piterskii, V. A. Selenznev, and A. V. Artemov, *Neftekhimiya*, **15**, 403 (1975).

9) Y. Kamiya and K. U. Ingold, *Can. J. Chem.*, **42**, 1027 (1964).

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

11) T. Matsuzaki, J. Imamura, and N. Ohta, *Kogyo Kagaku Zasshi*, **71**, 700 (1968).

12) J. Manassen, *Catal. Rev.-Sci. Eng.*, **9**, 223 (1974).

13) H. B. Knight and D. Swern, *Org. Synth.*, **34**, 90 (1954).

14) W. O. Lundberg, "Autoxidation and Antioxidants," Vol. 1, Interscience Publication, New York (1961), p. 375.

15) L. Horner and W. Jurgeleit, *Justus Liebigs Ann. Chem.*, **591**, 138 (1955).

16) D. A. S. Ravens, *Trans. Faraday Soc.*, **55**, 1768 (1959).

17) Y. Kamiya, "Yuki-Sanka-Hanno," Gihodo, Tokyo (1973), p. 244.

18) T. Yamada and Y. Kamiya, presented at the 9th Symposium on Oxidation, Tokyo, Japan, November 25, 26 (1975).

19) G. C. Allen and A. Aguilo, "Oxidation of Organic Compounds," Vol. 2, Am. Chem. Soc. (1968), p. 63.

20) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley & Sons, New York (1967), pp. 80—88, 124—246, 454—525.

21) J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reaction of Transition-Metal Complexes," Elsevier Publishing Company, Amsterdam, London and New York (1968).

22) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," A Comprehensive Text, Interscience Publication, New York (1966).

23) K. Yamazaki, N. Tanaka, J. Matsuura, and R. Tamamushi, "Muki-Yoeki-Kagaku," Nankodo, Tokyo and Kyoto (1968), pp. 14—26, 69—97, 268—271.

24) L. E. Orgel, "An Introduction to Transition-Metal

Chemistry," John Wiley & Sons, New York (1966).

25) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

26) A. H. Turner and W. A. Waters, *J. Chem. Soc.*, **1954**, 580; **1956**, 879.

27) C. F. Cullis and A. J. Waddington, *Trans. Faraday Soc.*, **53**, 1317 (1957).

28) R. Tsuchida, S. Yamada, and H. Nakamura, *Nature*, **178**, 1192 (1956).

29) R. L. Martin and A. Whitley, *J. Chem. Soc.*, **1958**, 1394.

30) J. K. Kochi and R. U. Subramanian, *Inorg. Chem.*, **4**, 1527 (1965).

31) S. Imamura, M. Teramoto, T. Sumi, and Y. Takegami, presented at the 8th Symposium on Oxidation, Osaka, Japan, November 21, 22 (1965).

32) L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 457, 2736 (1953).

33) R. M. Izatt, W. C. Fernelius, C. G. Haas, Jr., and B. P. Block, *J. Phys. Chem.*, **59**, 170, 235 (1955).