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The Liquid Phase Oxidation of Acrolein. IV.[*1] A Postulated Configuration of the Divalent Cobalt Acetylacetonate Catalysts in the Initiation Reaction

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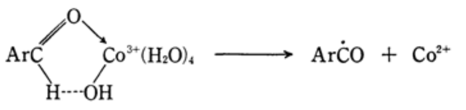
A possible configuration of the pale blue precipitated divalent cobalt catalyst, synthesized by the addition of a saturated solution of deionized water in acrolein to a vigorously stirred solution of $Co(acac)_2$ in benzene, is deduced from the infrared spectrum and thermal analyses; it is considered to be $Co(acac)_2$-H_2O-acrolein, in which acrolein is coordinated through its aldehyde oxygen. When the precipitated catalyst is used in the oxidation of acrolein, the induction period of oxygen absorption is shorter, the rate of oxygen absorption is higher, and the amount of oxygen absorbed is more than when any other divalent cobalt-acetyl-acetonate are employed. From these results, it is considered that the precipitated catalyst contains a species which is converted into a more active trivalent form faster than the other divalent catalysts. Furthermore, $Co(acac)_2$ and $Co(acac)_2\cdot 2H_2O$ are considered to take part in the oxidation *via* $Co(acac)_2$-H_2O-acrolein.

A liquid-phase oxidation of acrolein has already been investigated with metal naphthenates and acetylacetonates in various solvents.[1-3] The rate of oxygen absorption, $-dO_2/dt=k(\text{catalyst})^{0.5}\cdot(O_2)^{1.04}$, and other experimental results suggest the occurrence of the chain initiation reaction, which is an example of the general oxidation of aldehydes and which is expressed as follows:[4]

$$CH_2{=}CHCHO + Co^{3+} \longrightarrow CH_2{=}CH\dot{C}O + Co^{2+} + H^+.$$

A trivalent cobalt catalyst was most effective in initiating the reaction.[3] Waters and Bawn proposed that, in the liquid-phase oxidation of aldehydes, the initiation reaction was induced by a trivalent cobalt catalyst, in which the catalyst contained the aldehyde as a ligand in the transition state as follows:[5]

$$ArCHO + Co(OH)(H_2O)_5 \longrightarrow$$



However, the intermediate was not separated, nor was it ascertained accurately. In our investigation,[3] the structure of the cobalt catalyst during the reaction with cobalt acetylacetonates was also elucidated from the visible light spectra, the magnetic susceptibility, the molecular weight, and so on. From these results, the effective cobalt catalyst was found to have a six-coordinated trivalent configuration, and to have acrolein and water in addition to acetylacetone as ligands.

In this paper, new findings on the cobaltous catalyst, which was synthesized by the addition of a mixture of acrolein and water to a vigorously stirred solution of the catalyst of a cobaltous catalyst, $Co(acac)_2$, in benzene, are described. A possible configuration of the synthesized catalyst is considered on the bases of the IR spectra and the thermal analyses. Furthermore, the action of the catalyst in the liquid-phase oxidation of acrolein is discussed.

Experimental

Spectral Measurements. A Hitachi Model EPI-S2 infrared spectrometer was used to obtain absorption spectra in the range from 4000 to 700 cm^{-1}. The KBr disk method was employed for the preparation of the sample. The frequency reading was calibrated by the use of a polystyrene film.

Thermal Analyses. Thermal analyses were carried out using a thremal balance of the Oyorikagaku Co., Ltd., and a differential thremal analyzer of the Rikagaku Denki Co., Ltd.

Materials. The commercial acrolein (from the Shell Chemical Corp.) has a gas chromatographical purity of 95% by weight. The major impurities were propionaldehyde (3.5%), acetaldehyde (0.7%), acetone, a small amount of water, and an antioxidant (0.1% hydroquinone). Crude acrolein was distilled with a

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[*1] Part III: This Bulletin, **40**, 1893 (1967).

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2) W. F. Brill and F. Lister, *J. Org. Chem.*, **26**, 565 (1961).

3) A. Misono, T. Osa, Y. Ohkatsu and M. Takeda, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 2129 (1966).

4) C. H. Bawn, *Discussions Faraday Soc.*, **14**, 181 (1953).

5) T. A. Cooper and W. A. Waters, *J. Chem. Soc.*, **1964**, 1538.

distillator composed of 30 theoretical plates. All the impurities except propionaldehyde could be removed by this distillation. This acrolein still, however, contained a small amount of water, which was removed by shaking with an equal volume of anhydrous calcium sulfate for 30 min. Then the resulting acrolein was distilled again just before use, bp 52.5—52.9°C.

The benzene used as a solvent was purified by a conventional method.

Catalysts. Co(acac)$_3$, Co(acac)$_2$, and Co(acac)$_2$-2H$_2$O were prepared and purified by methods described in the literatures.[6,7] The cobaltous catalyst (hereinafter termed the precipitated catalyst) was prepared as follows. A saturated solution of 1.5 g of deionized water in 7.5 g of acrolein was added to a solution of 1.0 g of Co(acac)$_2$ in benzene in a 300m*l* dropping funnel. The resulting mixture was thoroughly mixed, and the pale blue precipitates were separated and dried under a vacuum.

Procedure. The reaction was carried out using a gas-sealed system with an oxygen-recycling unit, as is shown in Fig. 1. The system was composed of reactor (1), a gas inlet (2), a gas outlet (3), a magnetic stirrer (4), a water-cooled condenser (5), a dry ice-methanol-cooled condenser (6), a carbon dioxide-elimination tube (7), a gas-recycling pump (8), a gas holder (9), and a gas burette (10). The inside of the reaction system was purged with oxygen. Benzene and freshly-distilled acrolein were charged into the reactor in the ratio of 4 : 1 by volume, and then a known quantity of a catalyst was added. Immediately thereafter, oxygen was bubbled into the reaction solution by the pump at a flow rate of 200 m*l*/min at 25°C, thus starting the reaction. The stirring speed was maintained at 1000 rpm, since no effect of stirring on the reaction rate was observed over 600 rpm. The unreacted and undissolved effluent oxygen flowed out from the reactor with acrolein, benzene, and the other products into the water-cooled condenser, where the benzene was condensed and returned to the reactor. Then the gas mixture was passed through the second condenser, where the acrolein was condensed; through the carbon dioxide-elimination tube into the gas holder, and again recycled by the pump into the reactor. The amount of oxygen consumed was occasionally measured, and the same amount of new oxygen was charged into the system in order to keep the inside pressure at one atm. In the above procedure, the precipitated catalyst was too insoluble in many kinds of organic solvents to be refined by recrystallization. Therefore, the amount of the catalyts used was based on its metal content (6.38 wt%), and the catalyst was utilized as a suspension.

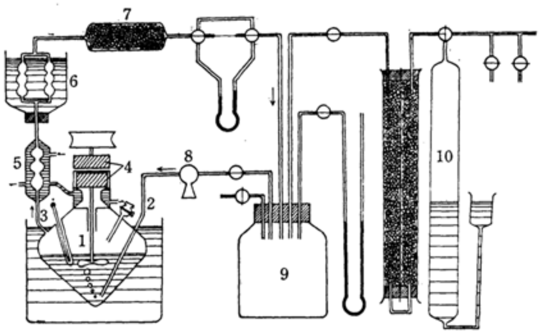

Fig. 1. Oxidation apparatus.

Results and Discussion

The amount of oxygen absorbed during the liquid-phase oxidation of acrolein with the precipitated catalyst, compared with Co(acac)$_3$, Co(acac)$_2$, and Co(acac)$_2$·2H$_2$O, is shown in Fig. 2. Defining the induction period as the time which elapses before the beginning of oxygen absorption, it was shorter for the precipitated catalyst than for any other cobaltous catalyst, in spite of

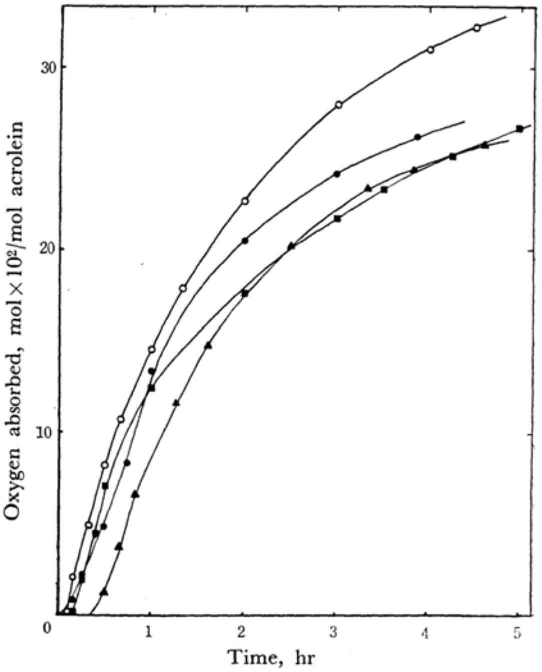

Fig. 2. Amount of oxygen absorbed.
Acrolein 10 m*l*; Benzene, 40 m*l*;
Temperature, 25°C;
Catalyst concentration, 1×10^{-3} mol/mol acrolein
○, The precipitated catalyst;
▲, Co(acac)$_2$; ■, Co(acac)$_2$·2H$_2$O
●, Co(acac)$_3$

Table 1. Induction periods of oxygen absorption

Catalyst	Induction period* min
The precipitated catalyst	6
Co(acac)$_2$·2H$_2$O	10
Co(acac)$_2$	24
Co(acac)$_3$	3

* Reaction conditions were the same as in Fig. 2.

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6) W. C. Fernelius and B. E. Bryant, *Inorganic Syntheses*, **5**, 188 (1957).
7) R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 440 (1958).

TABLE 2. IR SPECTRA OF ACROLEIN AND DIVALENT COBALT-ACETYLACETONATE CATALYSTS

Predominant modes of acrolein	Acrolein (liq.) cm^{-1}	Precipitated catalyst cm^{-1}	$Co(acac)_2$ cm^{-1}	$Co(acac)_2\cdot 2H_2O$ cm^{-1}	Predominant modes of acetylacetone
	733	730			
		761	762	781	CH out plane def.
		831			
CH_2 out of plane def.	914	899			
		935	931	934	CCH_3 + C=O str.
CH(ald.) def.	971	966			
		991			
CH out of plane def.	991	1069	1020	1020	CH_3 rock.
	1153	1150			
		1199	1199	1201	CH in plane bend.
		1240	1261	1268	CC str. + CCH_3 str.
	1272	1240			
Conjugated aldehyde	1361	1359			
		1381	1398	1402	CH_3 def.
CH_2 in plane def.	1402 1421	1430			
CH band. ?	1488	1462	1461	1462	CH bend.
		1512	1513	1521	C=O str.
		1569	1601	1610	C=O str. + C=C str.
C=C str.	1616	1649			
C=O str.	1675	1694			

the induction period being longer than for $Co(acac)_3$, as is shown in Table 1.

The oxygen absorption rates were calculated by a tangential method from the curves of Fig. 2; they are plotted in Fig. 3. The rate of oxygen absorption with the precipitated catalyst was highest in all the divalent cobalt-acetylacetonate catalysts at the beginning of the reaction, but it soon became small. Moreover, the amount of oxygen absorption with the precipitated catalyst was more than with any other catalysts (Fig. 2). Therefore, the precipitated catalyst is considered to change into a more active trivalent form faster than the other divalent catalysts. In other words, it may have a preferable configuration which is most easily converted into an active trivalent one in all the divalent catalysts used, resulting in the shortest induction period and the highest reaction rate.

It seems of great interest to discuss the possible configuration of the precipitated catalyst and its effectiveness in the oxidation of acrolein. The precipitated catalyst was found to coordinate acrolein and water from its IR spectrum (Fig. 4 and Table 2), which showed different absorptions from those of acrolein and divalent cobalt catalysts. The infrared spectra of acrolein and $Ni(acrolein)_2$, Schrauzer reported[8] a possible configuration of a nickel-acrolein complex by studying its IR spectra.

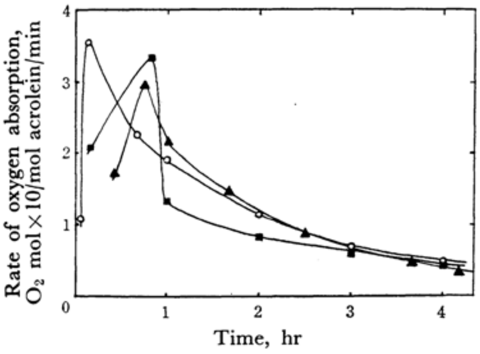

Fig. 3. Oxygen absorption rates.
Acrolein, 10 ml; Benzene, 40 ml;
Temperature, 25°C
Catalyst concentration, 1×10^{-3} mol/mol acrolein
○, The precipitated catalyst;
▲, $Co(acac)_2$; ■, $Co(acac)_2\cdot 2H_2O$

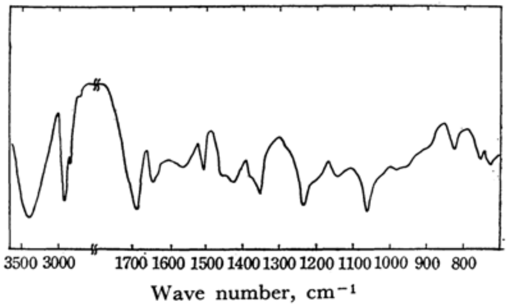

Fig. 4. IR spectrum of the precipitated catalyst.

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[8] G. N. Schrauzer, *Chem. Ber.*, **94**, 650 (1961).

produced from nickel tetracarbonyl and acrolein, were compared. The characteristic band of the aldehyde group of acrolein at about 2700 cm^{-1} disappeared in Ni(acrolein)$_2$, whereas the $C=O$ frequency of 1675 cm^{-1} of acrolein shifted to 1518 cm^{-1} in the complex. Moreover, the absorption of the $C=C$ bond was shifted from 1616 cm^{-1} to 1605 cm^{-1}. Furthermore, the frequencies of Ni(acrolein)$_2$ were compared with those of Ni(acrylonitrile)$_2$, and the possible configurations, shown in Fig. 5, were considered.

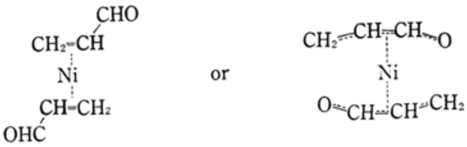

Fig. 5. Configuration of Ni(acrolein)$_2$.

The precipitated catalyst in our investigation showed in its infrared spectrum that the $C=C$ frequency shifted from 1616 cm^{-1} to 1649 cm^{-1}, while the $C=O$ frequency shifted from 1675 cm^{-1} to 1694 cm^{-1}. Since the absorption bands of 1649 and 1694 cm^{-1} did not exist in Co(acac)$_2$ and Co(acac)$_2\cdot$2H$_2$O, these may be ascribed to the acrolein in the precipitated catalyst. That is, this means that the catalyst coordinated acrolein as a ligand. However, in this case it should also be noted that the direction of the shifts was opposite to that reported by Schrazuer.

The attachment of nitrile ligands to metal by way of the nitrogen lone pair has been reported by many workers.[9-12] According to Kern,[13] the $-C\equiv N$ stretching bands of propionitrile and acrylonitrile complexes of metal chlorides in the first transition series shift to frequencies higher by 30—50 cm^{-1} in the complexes. Ross *et al.* also presented[14] the evidence from infrared and proton magnetic resonance spectroscopic studies for the attachment of acrylonitrile and acetonitrile through the nitrogen lone pair in $(CH_2CHCN)M(CO)_5$ $(M=W)$ and $(CH_2CHCN)_2M(CO)_4$ $(M=Cr, Mo, W)$. In this case, the nitrile stretching frequencies are shifted to a position higher than that in free acrylonitrile and acetonitrile, through the multiple carbon-carbon bond absorption of the former is essentially unchanged from its position of acrylonitrile itself. In the previous complexes,[15,16] the $C=C$ stretching vibration has been observed to shift to a lower frequency, analogous to the observations for olefin-metal complexes. In the nitrile complex, however, the nitrile-stretching absorption is shifted to a frequency higher by 20—30 cm^{-1} than that in the free ligand, indicating metal-to-ligand bonding by way of the lope pair of the nitrogen.[17-20]

The characteristic bands of the vinyl group of acrolein itself were 914, 991, 1421, and 1616 cm^{-1}, but those of the precipitated catalyst were changed to 889, 991, 1430, and 1649 cm^{-1}. The aldehyde group had its absorption at 1270 and 1675 cm^{-1} in acrolein, but at 1240 and 1694 cm^{-1} in the precipitated catalyst. The shifts of each absorption cannot be discussed without more detailed spectroscopic studies, because the transfer of electrons between the metal of the catalyst and acrolein as a ligand has not yet been clarified. However, the absorption bands of 1616 and 1675 cm^{-1}, which are recognized as bands of conjugated vinyl and carbonyl groups respectively, shifted to 1645 and 1694 cm^{-1}. These shifts to higher wave numbers suggest that acrolein is not coordinated with metal in the π-allyl configuration or through its carbon-carbon double bond, but through its oxygen lone pair. This consideration may be supported by the finding that the direction of the shifts of the acrolein ligand was opposite to that reported by Suhrauzer[8]; the many descriptions of shifts to higher $-C\equiv N$ frequencies in acrylonitrile complexes can be taken as indicating metal-to-ligand bonding by way of the lone pair of the nitrogen, because acrolein resembles acrylonitrile in configuration and electron distribution.

Furthermore, this consideration seems to be in good agreement with the results of that investigation[21] in which the carbonyl stretching frequency of propargyl undecynoate was shifted to a position higher by 15 cm^{-1} than that in the free one in a reaction with nickel tetracarbonyl, indicating metal-to-ligand bonding through the lone pair of the oxygen. It should be added here there have been a large number of observations and much speculation on 1 : 1 addition complexes of ketones and aldehydes with organo-magnesium compounds through their carbonyl groups in earlier literature.[22,23] Recently, Smith[24] offered convincing evidence from an ultraviolet spectroscopic study for the existence of 1 : 1 adducts. Becker[25]

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Table 3. Thermal analyses of the precipitated catalyst

Temperature °C	$Co(acac)_2 2H_2O$ Diff. therm. analysis	Precipitated catalyst: Diff. therm. analysis	Precipitated catalyst: Therm. balance*	Compound eliminated
84		○	28.5 mg	Acrolein
127	○			Hydrated water
134		○	10.5 mg	Hydrated water

* The reduced weight of 193.1 mg the catalyst employed.

reported spectral evidence for a complex of $MgBr_2$ with benzophenone, but the addition of methyl magnesium bromide regenerated the ketone spectrum.

The precipitated catalyst had not only all the absorption bands of acetylacetonate present in $Co(acac)_2$ and $Co(acac)_2 \cdot 2H_2O$, but also those of water like the latter (3000—3500 cm^{-1}). The catalyst was analyzed with an automatic thermal balance and an automatic differential thermal analyzer (Fig. 6 and Table 3). The curve from a thermal balance had obscure inflection points in changes in the sample weight in the temperature region between 50 and 100°C, but the thermal differential curve showed a thermal change at 84°C. These data are shown in Table 3, with those of $Co(acac)_2 \cdot 2H_2O$. The endothermic change at 84°C denotes the elimination of acrolein from the catalyst, while the change at 134°C represents that of the hydrated water. The temperature of 134°C was much higher than the temperature, 127°C, for the elimination of the hydrated water from $Co(acac)_2 \cdot 2H_2O$. These eliminations were ascertained by a study of the IR spectra, and the precipitated catalyst after the above analysis was identified with Co(acac).

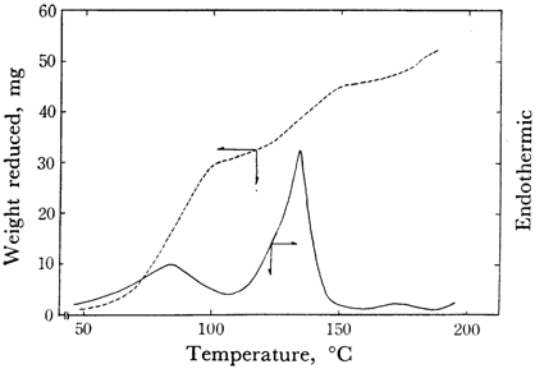
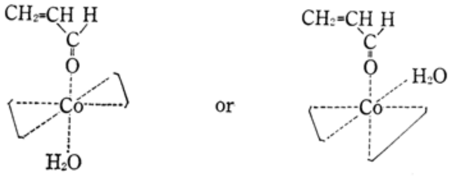


Fig. 6. Thermal analyses of the precipitated catalyst.
----, Thermal balance curve
——, Differential thermal curve

The ligands of $Co(acac)_2$ were found to be very stable, since a ligand exchange did not occur even if a mixture of $Co(acac)_3$, acrolein, and water stood under nitrogen atmosphere. It may, therefore, be estimated that acrolein and water in the precipitated catalyst were coordinated not by the ligand exchange with acetylacetone, but by the increase in the number of coordination sites of $Co(acac)_2$ from four to six. The Co:water:acrolein ratio in the precipitated catalyst is calculated to be about 1 : 1 : 1 from the results of the thermal balance shown in Table 3.

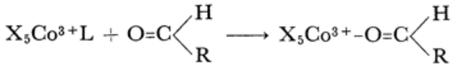
From the above findings and results, several possible configurations of the precipitated catalyst may be proposed, as in Fig. 7.



(I) (II)

Fig. 7. Configuration of the precipitated catalyst.
(I), Trans-form; (II), Cis-form;
╲——╱, Acetylacetone ligand

In the oxidation of aldehydes, Waters[26] and Bawn[37] proposed that the catalyst in the initiation reaction coordinates an aldehyde through its carbonyl group as a ligand as follows:



$$X_5Co^{3+}L + O{=}C\begin{smallmatrix}\diagup H\\ \diagdown R\end{smallmatrix} \longrightarrow X_5Co^{3+}{-}O{=}C\begin{smallmatrix}\diagup H\\ \diagdown R\end{smallmatrix}$$

This mechanism is generally and widely recognized. This may support the possible configuration of the precipitated catalyst shown in Fig. 7, because it is considered to be most easily converted into a trivalent catalyst of all the divalent cobalt catalysts employed and so may initiate the oxidation reaction. However, it should be understood that the accurate configuration can be determined only after more detailed investigations by the separation of the pure catalyst.

Conclusion

The liquid-phase oxidation of acrolein is initiated by an interaction of acrolein with a trivalent

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26) W. A. Waters *et al.*, *J. Chem. Soc.*, **1962**, 965; **1962**, 971; **1963**, 1538; **1964**, 2552; **1964**, 2560.
27) C. H. E. Bawn *et al.*, *Proc. Roy. Soc.*, **237A** 313 (1956); *Discussions Faraday Soc.*, **14**, 181 (1953).

cobalt, $Co(acac)_3$, that is, according to the following equation:

$$CH_2{=}CHCHO + Co^{3+} \longrightarrow CH_2{=}CH\dot{C}O + Co^{2+} + H^+.$$

In this case, acrolein and the catalyst must coexist within the distance in which an electron can transfer from the former to the latter. In other words, it is necessary that acrolein be coordinated to some extent with the metal of the catalyst, as has been reported by Waters and Bawn.

The pale bule catalyst was synthesized by the addition of a saturated solution of deionized water in acrolein to a vigorously stirred solution of $Co(acac)_2$ in benzene and was identified, from a study of the infrared spectrum and from thermal analyses, as $Co(acac)_2$-H_2O-acrolein, in which acrolein was coordinated through its carbonyl group. The use of this catalyst in the oxidation of acrolein resulted in the shortest induction period and in the highest rate of oxygen absorbed. That is, the ease of initiating the reaction and the rate of oxygen absorption were in the following ordres:

$Co(acac)_2$-H_2O-acrolein $<$ $Co(acac)_2 \cdot 2H_2O \ll Co(acac)_2$, and $Co(acac)_2 \approx Co(acac)_2 \cdot 2H_2O \ll Co(acac)_2$-$H_2O$-acrolein, respectively. From these results, it may be considered that the precipitated catalyst contains a species which is converted into a more active trivalent form faster than other divalent catalysts. Furthermore, the general interpretation that the coordination of a compound with a metal is more promoted in the hydrated complex than in the anhydrous complex supports the idea that $Co(acac)_2$ and $Co(acac)_2 \cdot 2H_2O$ take part in the oxidation *via* $Co(acac)_2$-H_2O-acrolein. This consideration may well explain the results obtained using three kinds of divalent cobalt catalysts.