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# The Liquid Phase Oxidation of Acrolein. V.[*1] Effects of Water on the Oxidation of Acrolein

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Some water was added as a model to a reaction solution containing $Co(acac)_2$ before the beginning of the reaction by two methods in order to examine the effects of water formed during the reaction. These two methods gave different phenomema in the induction periods and different oxygen absorption rates. From these results and those with $Co(acac)_2 \cdot 2H_2O$, the water added is considered to act in two ways, increasing the reaction rate by the coordination with the catalyst and decreasing the reaction rate when not bonded with the catalyst. The latter effect is considered in detail on the basis of the oxygen absorption rate: $-dO_2/dt=k(\text{acrolein})^{0.88} \cdot (\text{catalyst})^{0.39}(H_2O)^r$, wherein $r$ is $-0.1$ or $-0.21$. This rate equation accorded well with the derived rate equation considering the reaction phenomena and the interaction among the catalyst, acrolein, and water in the initiation reaction.

A small amount of water is formed in general autoxidations. It is very important, from both fundamental and industrial viewpoints, how the water formed affects the course of oxidation reactions. However, no systematic attempt to study this has been reported in the literature. Some reports[1-3] only briefly mention that a trace of water makes catalysts more soluble and, consequently, makes the reaction faster, whereas a greater amount of water deactivates catalysts.

In the case of the liquid-phase oxidation of acrolein, we have already reported that a catalyst activates the reactants and accelerates the reaction. The reactants, such as acrolein and peroxy acrylic acid, are coordinated with the catalyst and much activated.

The oxidation of acrolein with $Co(acac)_2$, $Co(acac)_2 \cdot 2H_2O$, or the precipitated catalyst synthesized from $Co(acac)_2$, acrolein and water, was investigated.[4] The precipitated catalyst was most effective in the initiation reaction in all the

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[*1] Part IV: Y. Ohkatsu, T. Osa and A. Misono, Reference 5.

1) C. H. E. Bawn and J. B. Williamson, *Trans. Faraday Soc.*, **47**, 721, 735 (1951).

2) Y. Kamiya and K. U. Ingold, *Can. J. Chem.*, **41**, 2034 (1963).

3) N. Michaels, Univ. Microfilms, University of Michigan, Ann Arbor, Mich. Order Order No. 61-5525.

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

divalent cobalt catalysts used, and its configuration was postulated to be Co(acac)$_2$-$H_2O$-acrolein.

In this paper, in order to examine systematically the effects of water formed during the oxidation reaction, the liquid-phase oxidation of acrolein in benzene with some catalysts, such as Co(acac)$_2$ and Co(acac)$_2$·$2H_2O$, was carried out, and some water was added as a model to the reaction solution before the beginning of the reaction. The effects of the amounts of water present on the oxidation reaction and on the activities of the catalysts will be discussed. Furthermore, difference between the effects of free water and of hydrated water will also be discussed.

## Experimental

**Spectral Measurements.** A Hitachi Model EPI-S2 infrared spectrometer and a Hitachi Model EPS-2 spectrometer were used in obtaining the infrared and near infrared spectra.

**Materials.** Commercial acrolein and benzene were used after purification by conventional methods to remove water and other impurities.

**Catalysts.** Co(acac)$_2$ and Co(acac)$_2$·$2H_2O$ were prepared by methods described in the previous paper.⁴⁾

**Apparatus.** The reaction apparatus described in the previous paper was used.*¹⁾

**Procedure.** The reaction was carried out according to the method described in the previous paper except that three different methods for charging reactants into the reactor were used. The three charging methods were as follows:

(1) When water was added to the reaction mixture:

The order (A): A mixture of the catalyst, Co(acac)$_2$, benzene, and water was first stirred vigorously in the reactor under an oxygen atmosphere for twenty minutes, and then acrolein was added to the mixture.

The order (B): A mixture of the catalyst and benzene was prepared in the reactor under an oxygen atmosphere, while, a mixture of acrolein and water was prepared elsewhere. The latter mixture was then added to the former.

(2) When no water was added to the reaction mixture:

A catalyst was dissolved into benzene in the reactor under an oxygen atmosphere. Acrolein was charged into the resulting solution.

## Results and Discussion

It has been reported⁵⁾ that the trivalent cobalt had the shortest induction period of all the cobalt acetylacetonate catalysts used in the liquid-phase oxidation of acrolein, which was induced through the following equation:

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

When a divalent cobalt catalyst was used, the induction period became longer than that of the trivalent catalyst; the difference between the induction periods with di- and trivalent catalysts was explained in terms of the period necessary for the conversion of the divalent catalyst into a trivalent catalyst. The periods with various catalysts were compared in the presence or in the absence of acrolein (Table 1).

TABLE 1. INDUCTION PERIODS WITH COBALT CATALYSTS

| Catalyst | Induction period | |
|---|---|---|
| | In presence of acrolein*, min | In absence of acrolein,** hr |
| Co(acac)$_2$ | 24 | 6 |
| Co(acac)$_2$·$2H_2O$ | 10 | 2 |
| Co(acac)$_2$-$H_2O$-acrolein | 6 | 0.5 |

* Experiments under the same conditions as described in the previous report.

** Experiments under the same conditions as described above, except no acrolein was used. The values represent the periods till the reaction solutions acquired green color of a trivalent cobalt.

From the difference in induction periods between the divalent cobalt and the hydrated divalent cobalt, it was found that the latter changed into a trivalent cobalt faster than the former. The hydrating water of the catalyst is, therefore, considered to be a promoter of the conversion described

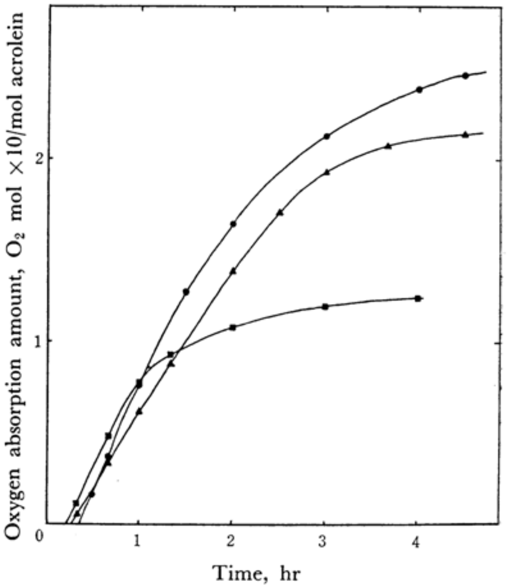

Fig. 1. Oxygen absorption amount in the oxidation of acrolein by addition of water (the order (A)).

Reaction conditions: acrolein, 10 m*l*; benzene, 40 m*l*; 25°C; water,

●, 1 mol/Co(acac)$_2$ mol

▲, 4 mol/Co(acac)$_2$ mol

■, 14 mol/Co(acac)$_2$ mol

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5) Y. Ohkatsu, T. Osa and A. Misono, This Bulletin, **40**, 2111 (1967)

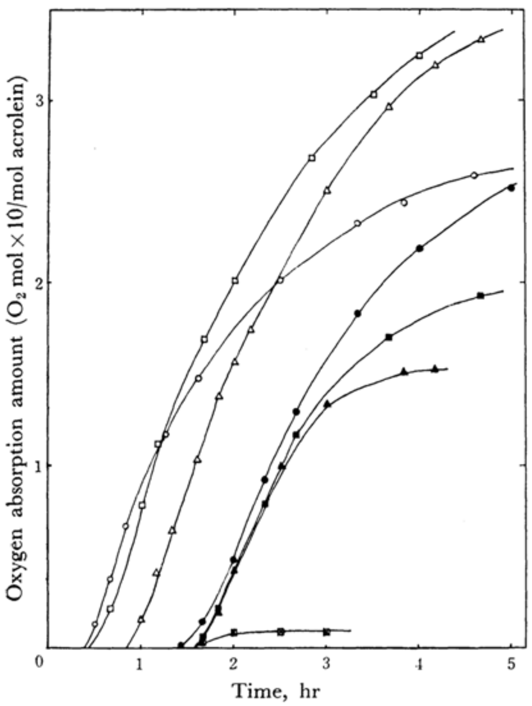


Fig. 2. Oxygen absorption amount in the oxidation of acrolein by addition of water (the order (B)).
Reaction conditions: acrolein, 10 m*l*; benzene, 40 m*l*; 25°C; water,
□, 1 mol/Co(acac)$_2$ mol
△, 2 mol/Co(acac)$_2$ mol
●, 4 mol/Co(acac)$_2$ mol
■, 6 mol/Co(acac)$_2$ mol
▲, 13 mol/Co(acac)$_2$ mol
⊠, 20 mol/Co(acac)$_2$ mol
○, Absence

above. Furthermore, the presence of acrolein also hastened the above change. These facts seem to support the finding that the Co(acac)$_2$-$H_2O$-acrolein catalyst described in the previous paper[5] has the shortest induction period of all divalent acetylacetonate catalysts.

The order of the addition of free water affected the oxidation reaction considerably. Figures 1 and 2 illustrate the amount of oxygen absorbed during the oxidation of acrolein in the order (A) and in the order (B) respectively. In the case of the order (A) (acrolein was added to a mixture of Co(acac)$_2$, benzene and water which had previously been stirred for twenty minutes), the total amount of oxygen absorbed was smaller when more water was added; the reaction solution became heterogeneous by the addition of six moles of water per mole of the catalyst, and the water added in excess of six times of the catalyst amount separated from the benzene solution. On the other hand, in the order (B) (a mixture of acrolein and water was added to a mixture of the catalyst and benzene), when one or two moles of water were added, the total amount of oxygen absorbed was larger by one-third than that with Co(acac)$_2$, but the amount became smaller when more water was added. The reaction solution was homogeneous even if more than six moles of water per mole of the catalyst were added, but the catalyst precipitated when more than thirteen moles of water per mole of the catalyst was added; these phenomena were not observed when the order (A) was used.

Figure 3 shows the induction periods *versus* the amount of water added. The filled circles and open circled denote the results of the order (A) and the order (B) respectively, and the ground line is based on the results without any added water. In the order (A), when water was added, the induction periods became shorter than that with Co(acac)$_2$ and approached the value obtained with Co(acac)$_2$·2$H_2O$. This fact suggests that Co(acac)$_2$ was partly (when one or two moles of water were added) or completely (when fourteen moles of water were added) converted into Co(acac)$_2$·2$H_2O$ during the vigorous stirring of the mixture of the catalyst, benzene, and water for twenty minutes before the reaction. This was ascertained by the fact that the infrared spectrum of the catalyst, recovered after the twenty-minute stirring and immediately dried by the evaporation of water and benzene in a vacuum, was identical with that of Co(acac)$_2$·2$H_2O$ (Fig. 4). In the order (B), on the other hand, the induction periods became longer when water was added, but the induction periods were almost constant when more than six moles of water per mole of the catalyst were used.

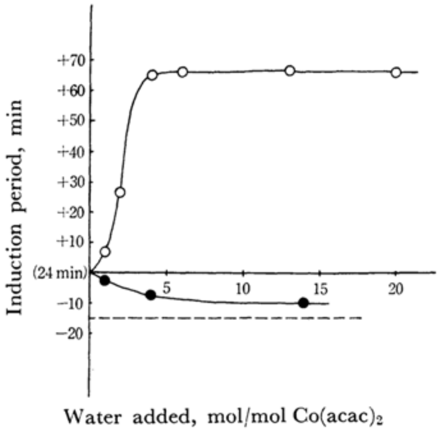


Fig. 3. Induction period based on the result without added water.
1) ——, ground line (induction period with Co(acac)$_2$)
2) - - -, induction period with Co(acac)$_2$·2$H_2O$
3) ●, the order (A) ○, the order (B)

Figure 5 shows the maximum oxygen absorption

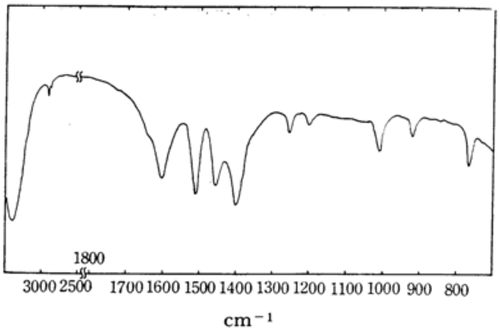


Fig. 4. IR spectra of the catalyst obtained from the reaction solution of the order (A) before the biginning of the reaction and $Co(acac)_2$, wherein the both spectra accorded with each other completely.

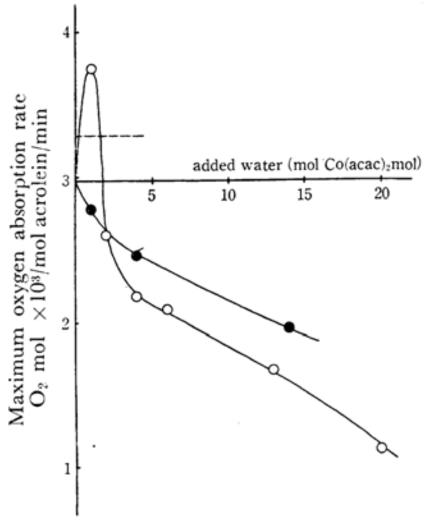


Fig. 5. Maximum oxygen absorption rate based on the result without added water.

1) ——, ground line (oxygen absorption rate with $Co(acac)_2$)
2) - - -, maximum oxygen absorption rate with $Co(acac)_2 \cdot 2H_2O$
3) ●, the order (A) ○, the order (B)

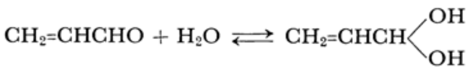
rates. In the case of the order (B), the maximum oxygen absorption rate was high when one mole of water per mole of the catalyst was added, whereas in the case of the order (A), it became smaller when more water was added.

It may be concluded from these findings that added water influences: (1) the oxygen absorption rates and the amount of oxygen absorbed, and (2) the induction periods, but that the action and the effects of added water are dependent upon the order of the addition of water.

The added water acted negatively in the order (A) in the oxidation of acrolein, whereas it acted either positively or negatively in the order (B). The positive effects in the order (B) are considered to be due to the presence of more active catalyst species than in the order (A), and may be estimated as follows. Sone⁶⁾ reported that $Co(acac)_2$ reacted readily with water to produce $Co(acac)_2 \cdot 2H_2O$, which dissolved less in non-polar solvents. Therefore, the so-called postulate that a trace of water makes the catalyst more soluble and that, consequently, the reaction rate increases, is not applicable to the order (B). Moreover, $Co(acac)_2 \cdot 2H_2O$ was not formed in the order (B), where the aspects of the reaction were different from those in the order (A) (Figs. 1, 2, 3, and 5). Thus, the addition of water may result in the formation of some compound which may increase the rate of the reaction. Examples of such compounds may be a water-acrolein complex or a water-acrolein-catalyst complex.

The previous paper⁵⁾ reported the synthesis of the $Co(acac)_2$-$H_2O$-acrolein under similar reaction conditions with the addition of twenty times as much water in the order (B), except that no oxygen was bubbled in and the benzene and water were evaporated off. It may be considered, therefore, that the catalyst, having the configuration of $Co(acac)_2$-$H_2O$-acrolein, was also formed by the addition of twenty moles of water in the order (B), but that the reaction rate was considerably smaller. This means that excess water which cannot be coordinated with the catalyst results in a decrease in the reaction velocity. That is to say, the addition of water acts in two ways, increasing the reaction rate by coordination with the catalyst and decreasing the rate when not bonded to the catalyst. This consideration accords with the findings that, in the absence of excess water, that is, in the addition of one mole of water, an active catalyst, such as $Co(acac)_2$-$H_2O$-acrolein, is present and increases the reaction rates that the catalyst, with which much oxygen is absorbed in spite of a decrease in the reaction rate, is formed by the addition of two moles of water, and that more water lessens both the oxygen absorption amount and the reaction rates.

Hence, orthoacrolein is a possible form of the acrolein-water complex:



$$CH_2{=}CHCHO + H_2O \rightleftarrows CH_2{=}CHCH\begin{cases}OH\\OH\end{cases}$$

However, the water content of the mixture formed by the drop-by-drop addition of water to acrolein was analyzed with a near-infrared spectrometer. As is hown in Fig. 6, water had three absorption bands and its spectra shows quantitatively that water added to dry acrolein existed in the form of water itself, and not as a complex with acrolein. That is, the free water added had no measurable interaction with acrolein.

More water than was soluble was added to the

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6) K. Sone, *Chemistry (Kagaku)*, **14**, 544 (1959).

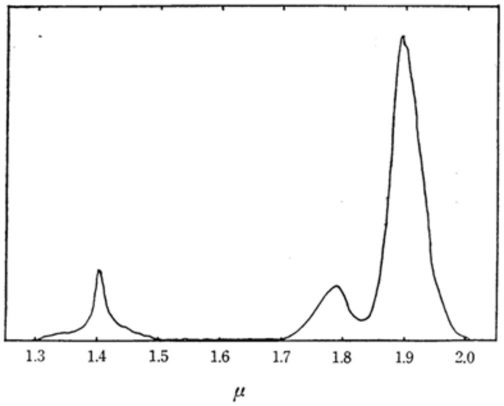

Fig. 6. Near-infrared spectrum of a mixture of acrolein and water.

benzene solution of a catalyst, and the resulting mixture was vigorously stirred. Water was found to adhere to the wall of the reactor with the catalyst by means of the centrifugal action of stirring. This means that free water tended to exist around the catalyst and was concentrated there. Since acrolein must be coordinated with the catalyst in order for the reaction to be initiated, acrolein must diffuse through the water layer to reach the coordination shell of the catalyst in the presence of the excess water. In the order (A), more water than six times the amount of the catalyst separated from the reaction solution and acrolein could approach the catalyst more easily than in the order (B), because in the former less water existed around the catalyst. Moreover, the initiation of the oxidation reaction was promoted a little by the easier coordination exchange of the hydrated water of the $Co(acac)_2 \cdot 2H_2O$ formed partly and completely with acrolein; thereafter the reaction proceeded smoothly. Therefore, induction periods became shorter as more water was added in the order (A). On the other hand, in the order (B) more water existed around the catalyst; moreover, competition for the coordination of acrolein and water must occur. Consequently, induction periods became longer when water was added.

Bawn1) added water to the oxidation reaction mixture containing acetaldehyde by means of measured volumes of a 10% solution of water in acetic acid. Measurements at constant aldehyde and cobalt acetate concentrations showed that, up to 3% of added water, the rate of the oxidation of acetaldehyde was inversely proportional to the water concentration, that is to say, $-dO_2/dt = \text{const.}/(0.2+(H_2O))$. The immediate oxygen uptake was not affected by the addition of water, but the sequent rate was much reduced. This suggests that water is not interfering with the oxidation chains, but only with the initiating reaction:

$$Co^{3+} + AcOOH \rightarrow Co^{2+} + AcOO\cdot + H^+$$

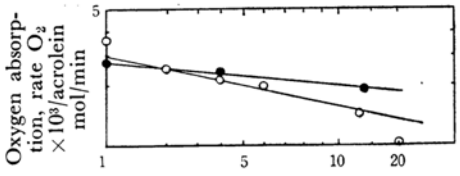

Fig. 7. Oxygen absorption rate *versus* amount of water added.
●, the order (A) ○, the order (B)

It is plausible that water tends to replace acetic acid in the coordination shell of the cobaltic ions to an extent depending on the water concentration, thereby impeding the above reaction.

In the oxidation of acrolein, the maximum oxygen absorption rate is given by the following equation, derived from the slopes of the lines in Fig. 7 and other experiments:

$$-dO_2/dt = k(\text{acrolein})^{0.88}(\text{catalyst})^{0.39}(H_2O)^r$$

in which the concentrations of acrolein range from 0.5 to 3.0 mol/*l*, the concentrations of the catalyst range from $5\times10^{-5}$ to $9.0\times10^{-4}$ mol/mol of acrolein, and the concentrations of water range from 1 to 14 mol per mole of the catalyst in the order (A) and from 2 to 13 mol per mole of the catalyst in the order (B). In the latter, the data from the addition of 1 and 20 mol of water were excluded because they were obtained in extraordinary reactions of the oxygen absorption. The effect of oxygen pressure was not studied in this investigation, but in the oxidation of unsaturated aldehydes almost a first order of oxygen pressure was reported.5,7) This may be adequate for these studies. In the above rate equation, $r$ was given as follows:

the order (A) $r = -0.1$
the order (B) $r = -0.21$

If the following steps are considered in this oxidation;

Initiation:

$$CH_2{=}CHCHO \xrightarrow{R_i} CH_2{=}CH\dot{C}O$$

Chain transfer:

$$CH_2{=}CH\dot{C}O + O_2 \xrightarrow{k_2} CH_2{=}CHCOO_2\cdot$$

$$CH_2{=}CHCOO_2\cdot + CH_2{=}CHCHO$$

$$\xrightarrow{k_3} CH_2{=}CHCOO_2H + CH_2{=}CH\dot{C}O$$

Termination:

$$2CH_2{=}CHCOO_2\cdot \xrightarrow{k_6} \text{inert compound}$$

the steady-state treatment of the overall reaction yields the expression:

$$-dO_2/dt = (k_3/k_6^{1/2})Ri^{1/2}(\text{acrolein})^{1.0}.$$

If the reaction is preferably induced by the catalyst

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7) W. F. Brill, *J. Org. Chem.*, **26**, 565 (1961).

of $Co(acac)_2$-$H_2O$-acrolein in the following equations:

$$Co^{2+} + H_2O + CH_2{=}CHCHO$$
$$\overset{K}{\rightleftharpoons} Co^{2+}(H_2O)(CH_2{=}CHCHO)$$
$$Co^{2+}(H_2O)(CH_2{=}CHCHO) + O_2$$
$$\xrightarrow{k_1} Co^{3+}(H_2O)(CH_2{=}CHCHO) + O_2^-$$
$$\xrightarrow{\text{fast}} Co^{2+}(H_2O) + CH_2{=}CH\dot{C}O$$

wherein the acetylacetone ligands of the catalyst are abridged, $R_i$ is given as $Kk_1(CH_2{=}CHCHO)$-$(Co^{2+})(H_2O)(O_2)$.

When acrolein approaches the catalyst through the water layer despite the repelling power of water and replaces water as the new ligand, water will act negatively against the approach of acrolein to the catalyst. That is, the concentration of acrolein ($Q$) approaching the catalyst is inversely proportional to the water concentration in the initiation reaction: $Q = Af(\text{acrolein})/g(H_2O)$, in which $A$ is a constant, $f$(acrolein) is a function of the concentration of acrolein to the catalyst, and $g(H_2O)$ is a function of the concentration of water around the catalyst.

Consequently, $R_i$ may be described as follows:

$$R_i = AKk_1(Co^{2+})(O_2)(H_2O/g(H_2O))(f(\text{acrolein}))$$

Therefore, the rate is expressed as:

$$-dO_2/dt = A^{1/2}(k_3K^{1/2}k_1{}^{1/2}/k_6{}^{1/2})(Co^{2+})^{1/2}$$
$$\times(H_2O/g(H_2O))^{1/2}$$
$$\times(\text{acrolein}\cdot f(\text{acrolein})^{1/2})(O_2)^{1/2}.$$

Hence, $f$(acrolein) is $(\text{acrolein})^{0-1.0}$, because $f$(acrolein) is equal to $(\text{acrolein})^{1.0}$ at most in the absence of water. Moreover, $(H_2O)^r$ is assumed in place of $(H_2O/g(H_2O))$. Furthermore, as $CH_2{=}CH\dot{C}O + O_2 \rightarrow$ is a rate-determining step in the oxidation of unsaturated aldehyde,7) the termination step is considered to contain:

$$2CH_2{=}CH\dot{C}O \longrightarrow \text{inert compound},$$

whereupon the order with respect to the oxygen increases above one half. Therefore, the above equation becomes:

$$-dO_2/dt = (k_3K^{1/2}k_1/k_6{}^{1/2})(Co^{2+})^{0.5}(H_2O)^r$$
$$\times(\text{acrolein})^{1.0-1.5}(O_2)^{0.5-1.5}.$$

The experimental equation may be compared with that derived from the postulated mechanism. As the catalyst was deactivated by the polymers formed during the oxidation, the order with respect to the catalyst decreases more in the empirical equation than in the derived one, as does the order of acrolein also.4) The order of the oxygen pressure accords with the results in other reports.4,7) The difference in the $r$ values in the orders (A) and (B) may arise from the different $g(H_2O)$ values, which indicate a function by which water interferes with the approach of acrolein to the catalyst, and the effect of $g(H_2O)$ in the order (B) is larger than that in the order (A) in the experimental equation. This was observed in the experiments, in which the excess water in the order (A) was separated from the reaction solution, but water was not separated in the order (B). Therefore, when $r$ represents $-0.1$ and $-0.21$ in the orders (A) and (B) respectively, the empirical equation may be approximately explainable by the assumed scheme.

From the results, it may be concluded that the water capable of bonding with the catalyst increases the reaction rate, while any other water decreases it.