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The Effect of Acetates on the Synthesis of Acetic Acid from Methanol and Carbon Monoxide in the Presence of Cobalt(II) Iodide as a Catalyst

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In the synthesis of acetic acid from methanol and carbon monoxide in the presence of cobalt(II) iodide as a catalyst, the addition of an acetate has been shown to have a great influence upon the methanol conversion into total acetic acid. When the added amounts of potassium acetate are from one to two times as much as that of cobalt(II) ion, both methanol conversion and its reaction rate reach a maximum, and methanol is prevented from forming dimethyl ether. On the other hand, the reaction nearly stops when the amount of potassium acetate becomes more than four times as large. The variation in the absorption spectrum of cobalt(II) ion in course of the reaction shows that the increase in the added amount of an acetate is favorable for the formation of cobalt carbonyls and that most cobalt(II) ions are tetrahedral species of the $[\text{Co(AcO)}_{4-n}\text{I}_n]^{2-}$ type so long as the reaction is promoted with the catalyst. From these experimental results, the course of the reaction has been discussed.

The reaction rate of the synthesis of acetic acid from methanol and carbon monoxide is promoted by the use of cobalt(II) iodide as a catalyst, a method which originated in Reppe's work.[1] The present authors have previously reported that, when a mixture of cobalt(II) acetate and an iodide[*1] was used as the catalyst, both the conversion of methanol into acetic acid and the absorption rate of carbon monoxide were always larger than in the case where only cobalt(II) iodide was used as the catalyst.[2] There is no difference in their components between cobalt(II) iodide and a mixture of cobalt(II) acetate and an iodide except that the latter contains acetates. In our last paper,[3] dealing with the variation in the absorption spectrum of cobalt(II) ion catalysts during the course of the reaction of methanol with carbon monoxide-hydrogen mixtures, it was shown that, when iodide ions were also present, most of the cobalt(II) ions did not form cobalt carbonyls, but tetrahedral species of the $[\text{Co(AcO}^{*2})_{4-n}\text{I}_n]^{2-}$ type. These facts suggest that an acetate should have some influence upon the methanol conversions into C_2-oxygenated organic compounds as well as on the absorption spectrum of cobalt(II) during the course of the reaction.

This work was undertaken in order to make clear the effect of an acetate, especially on the acetic acid synthesis reaction, and in order to study the behavior of cobalt(II) ion through recording its absorption spectrum.

Experiments

Apparatus for Carrying Out the Reaction.—The apparatus for carrying out the reaction was nearly the same as that described in previous papers.[2] The reaction vessels used were 180 ml. and 230 ml. vessels lined with a titanium manganese alloy. After a mixture of methanol, acetic acid and water containing a given amount[*3] of the catalyst had been placed in the vessel, carbon monoxide was introduced up to 50 kg./cm^2 at room temperautre. The mixture was then heated up to 210—215°C (the pressure became about 120 kg./cm^2) by a shaking type of electric furnace (60 r.p.m.) within 2 hr. After the temperature had been kept constant for about one hour., carbon monoxide of a higher pressure was introduced up to a definite reaction pressure (200—400 kg./cm^2) from a pressure accumulator. During the reaction, the pressure was kept constant by supplying carbon monoxide; the amount of it was measured in order to ascertain its absorption rate. The heating and additiob of gas were stopped after a predetermined time of the reaction, and then the vessel was allowed to cool to room temperature.

Apparatus for Taking the Absorption Spectra in the Course of the Reaction.—The special autoclave used for taking the absorption spectrum of the cobalt(II) ion catalyst during the course of the reaction was essentially the same as that described in the last paper, except that it was improved so as to endure pressures of 250—350 kg./cm^2 at 210°C. A solution of 2.5 ml. was placed in the special autoclave (6.0 ml. in vol.) with a couple of thick quartz windows, and then carbon

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[1] W. Reppe, *Ann. Chem. Jutus Liebigs*, **582**, 74 (1953).

[*1] LiI, NaI, KI, CaI^2 etc.

[2] T. Mizoroki, M. Nakayama, Y. Andō and M. Furumi, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **65**, 1049, 1054 (1962).

[3] T. Mizoroki and M. Nakayama, This Bulletin, **38**, 1876 (1965).

[*3] AcO=CH_3COO.

[*2] This is represented by the percentage composition in moles of the solution.

monoxide was introduced up to the pressure of 70—80 kg./cm² at room temperature. The autoclave was heated up to 21°C within one hour. After the temperature had been kept constant (±0.5°C) for about 20 min. by an electronic thermo-controller, carbon monoxide was introduced up to 300 kg./cm² and the absorption spectra were recorded by an automatic spectrophotometer from 340 mμ to 1000 mμ.

Materials.—The carbon monoxide and hydrogen were obtained from the decomposition of formic acid and the electrolysis of water respectively; they were compressed into the pressure accumulator. All of the other materials used were obtained from commercial sources.

Analytical Procedures.—The main components in the liquid products were determined by a gas chromatographic procedure. A 4.0 meter glass column or a 6.0 meter copper one with PEG-400 on a Diabase-A*4 was used at the temperature of 80°C, with the hydrogen carrier at the gas flow rate of 50 ml. per min. In this way, the amounts of methanol, methyl acetate and water in the liquid products obtained from the acetic acid synthesis were determined quantitatively,*5 using diethyl ketone as an internal standard substance. On the other hand, the amounts of dimethyl ether, acetaldehyde, methyl acetate, ethyl acetate, methanol, ethanol and water in the liquid products, obtained from the reaction of methanol with carbon monoxide and hydrogen mixtures, were determined by using pyridine as an internal standard, because it was difficult to separate diethyl ketone from ethanol by this gas chromatography. The amount of free acetic acid was determined by titration with an aqueous potassium hydroxide solution. The other analytical procedures were exactly the same as those used in previous papers.

Results and Discussion

The Effect of Acetates on the Methanol Conversion.—When a mixture of cobalt(II) acetate and an iodide is used as the catalyst in the reaction of methanol with carbon monoxide to form acetic acid, the presence of a relatively large amount of an iodide favors an increase in its rate.²⁾ When cobalt(II) iodide is used, however, neither the methanol conversion into total acetic acid (free acid and its ester) nor its rate increases, even if an iodide is added in considerable amounts. It was very difficult, therefore, to obtaine the most favorable mole ratio of iodide ions to cobalt(II) ions for this reaction. In all experiments, the I^-/Co^{2+} ratios present in the solutions used were always adjusted to be four by using proper amounts of cobalt(II) iodide and sodium iodide. Lithium acetate, sodium acetate, magnesium acetate or manganese(II) acetate was added as an acetate*6 to the solutions, although there were no differences in their effects. The effects of potassium propionate, sodium benzoate, sodium succinate, potassium isobutyrate and borax were examined at the same time in order to compare them with that of potassium acetate. The results are summarized in Fig. 1 and Table I. Both the absorption rate*7 of carbon monoxide and the methanol conversion into acetic

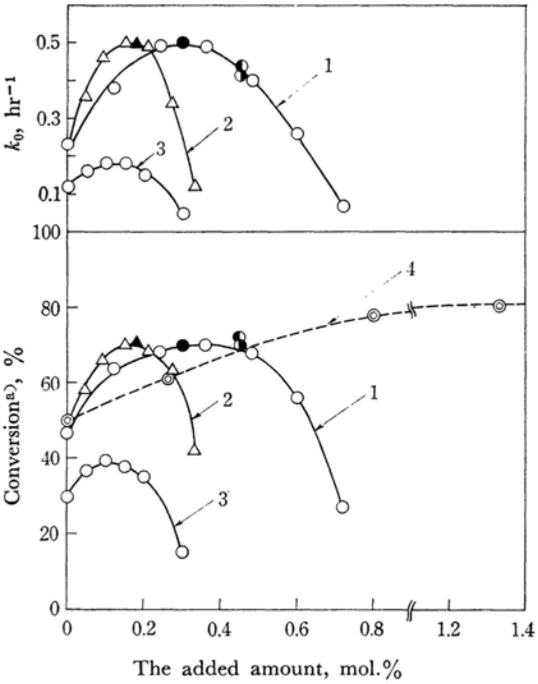

Fig. 1. The effect of an acetate on the acetic acid synthesis.

Curves 1 and 2: CH_3OH 1.80 mol. (54 mol.%), AcOH 0.20 mol. (6.0 mol.%), H_2O 1.33 mol. (40 mol.%), CoI_2 8.0 mmol. (0.24 mol.%), NaI 16 mmol. (0.48 mol.%); temp. 210—215°C, press. 350 kg./cm², time 2.5 hr.; ○ AcOK ◑ $(CH_3)_2CHCOOK$, ◐ C_6H_5COONa, ● C_2H_5COONa, △ $Na_2B_4O_7\cdot 10H_2O$, ▲ $C_2H_4(COONa)_2\cdot 6H_2O$

Curve 3: CH_3OH 1.80 mol. (54 mol.%), AcOH 0.20 mol. (6.0 mol.%), H_2O 1.33 mol. (40 mol. %), CoI_2 3.3 mmol. (0.10 mol.%), NaI 6.7-mmol. (0.20 mol.%); temp. 210—215°C, press. 300 kg./cm², time 2.5 hr.

Curve 4: $AcOCH_3$ 0.85 mol. (31 mol.%), AcOH 0.10 mol. (3.7 mol.%), H_2O 1.75 mol. (65 mol. %), CoI_2 7.2 mmol. (0.27 mol.%), NaI 14.4 mmol. (0.53 mol.%); temp. 210—215°C, press. 350 kg./cm², time 2.5 hr.

a) The acid acetic previously added to the solutions was excluded.

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*4 Prepared by The Kotaki Seisakusho Co., Ltd., Tokyo.

*5 Their errors were less than 3%.

*6 Nickel(II) acetate had no effect. Its dissociation is probably small.

*7 It is nearly in proportion to the total amounts of methanol and methyl acetate present in the autoclave. k_0 (hr.⁻¹) is the absorption rate constant of carbon monoxide at a constant temperature and pressure.²⁾ $dC/dt=k_1(1-C)$, where C is the methanol conversion into total acetic acid.

TABLE I. THE EFFECT OF POTASSIUM ACETATE AND BORAX ON THE ACETIC ACID SYNTHESIS AT VARIOUS PRESSURES

CH_3OH 1.35 mol. (43.2 g.), AcOH 0.15 mol. (9.0 g.), H_2O 1.00 mol. (18.0 g.), Purity of CO. 98%. Temp. 215°C, Time 2.5 hr. The added amount of catalyst (mmol.): (1) CoI_2 6.0, NaI 12.0. (2) CoI_2 6.0, NaI 12.0, AcOK 9.0. (3) CoI_2 6.0, NaI 12.0, $Na_2B_4O_7 \cdot 10H_2O$ 4.5. (4) $Co(AcO)_2 \cdot 4H_2O$ 6.0, NaI 24.0.

Press. kg./cm²	Cat.	The amounts of liq. prod., g.	Compositions of liq. prod., wt.%					Mass balance of CH_3OH,[a)] %		
			$(CH_3)_2O$	$AcOCH_3$	CH_3OH	H_2O	AcOH	Total AcOH	CH_3OH	Others[b)]
250	1	73.2	7.5	19.0	10.1	33.0	22.2	22.9	35.6	41.5
	2	88.5	1.6	29.6	11.6	26.3	23.6	40.8	50.9	8.3
	3	89.8	2.6	30.9	10.2	27.4	23.6	42.8	50.2	7.0
	4	89.9	—	29.1	11.4	26.5	23.9	41.6	50.8	7.6
300	1	83.1	8.4	21.8	7.0	30.4	30.6	38.5	34.5	27.0
	2	93.9	1.5	25.7	6.0	25.4	36.9	55.8	37.9	6.3
	3	96.0	1.4	26.3	6.7	25.1	36.4	57.3	40.4	2.3
	4	94.7	—	24.8	5.5	25.2	36.1	54.6	36.5	8.9
350	1	89.6	6.1	21.6	4.3	28.3	37.7	50.0	30.5	19.5
	2	97.7	0.8	20.1	2.9	22.0	47.7	66.2	26.8	7.0
	3	97.6	1.2	20.1	2.9	23.2	48.9	67.5	26.8	5.7
	4	98.3	—	17.7	2.4	21.8	50.0	67.0	23.9	9.1
420	1	97.3	2.6	16.8	2.0	22.1	50.8	66.4	22.2	11.4
	2	101.2	0.5	12.3	1.4	21.1	58.6	74.5	16.7	8.8
	3	99.3	0.4	14.2	1.5	20.3	57.6	73.5	18.5	8.0
	4	101.7	—	12.5	1.2	22.3	57.4	73.5	16.7	9.8

a) The acetic acid previously added to the solutions was excluded.
b) Most of them are dimethyl ether, methane and acetaldehyde.

TABLE II. THE EFFECT OF POTASSIUM ACETATE ON THE REACTION OF METHANOL WITH CARBON MONOXIDE - HYDROGEN MIXTURES

CH_3OH 1.35 mol. (43.2 g.), AcOH 0.15 mol. (9.0 g.), CoI_2 6.0 mmol., NaI 12.0 mmol., $CO/H_2 =$ 1.0, Temp. 200°C, Press. 400 kg./cm², Time 120 min.

The added amount of AcOK mmol.	The amount of liq. prod. g.	Mass balance of CH_3OH[a)] %						Conversion into C_2 %
		$(CH_3)_2O$	AcH	Total C_2H_5OH	Total AcOH	Total CH_3OH	Others[b)]	
0.0	75.0	9.9	4.5	4.5	10.4	25.8	44.9	19.4
3.0	77.3	5.8	3.6	3.7	10.3	33.0	43.6	17.6
6.0	82.6	1.0	5.0	13.8	13.7	26.7	39.7	32.5
9.0	86.2	0.9	4.5	19.3	15.6	33.5	26.2	39.4
12.0	86.8	0.9	3.7	24.0	15.6	37.7	18.1	43.3
15.0	78.5	0.3	10.4	14.7	13.7	46.2	15.0	38.5
18.0	60.5	—	—	—	8.5	88.5	3.0	8.5

Total $C_2H_5OH = C_2H_5OH + AcOC_2H_5$
Total $AcOH = AcOH + AcOCH_3 + AcOC_2H_5$
Total $CH_3OH = CH_3OH + AcOCH_3$
a) The acetic acid previously added to the solutions are excluded.
b) Most of them are crotonaldehyde, butylaldehyde, butanol, dimethyl acetal and methane and dimethy ether of the purged gases.

acid reach a maximum when the amount of potassium acetate added is from 1.0 to 2.0 times as much as that of cobalt(II) ions. However, the reaction nearly stops when it becomes more than four times as large. Nearly the same results are obtained by using other salts of carboxylic acid or borax in place of the acetates. The curve 4 in Fig. 1 is the result obtained from the reaction of methyl acetate with carbon monoxide, in which case methyl acetate was placed into the autoclave instead of methanol. It is different from the curves 1 and 2 in that the conversion of methyl acetate into acetic acid ($AcOCH_3 + CO + H_2O \rightarrow 2AcOH$) does not decrease with an increase in the amount of potassium acetate added. These salts also have a great influence on the reaction of methanol with

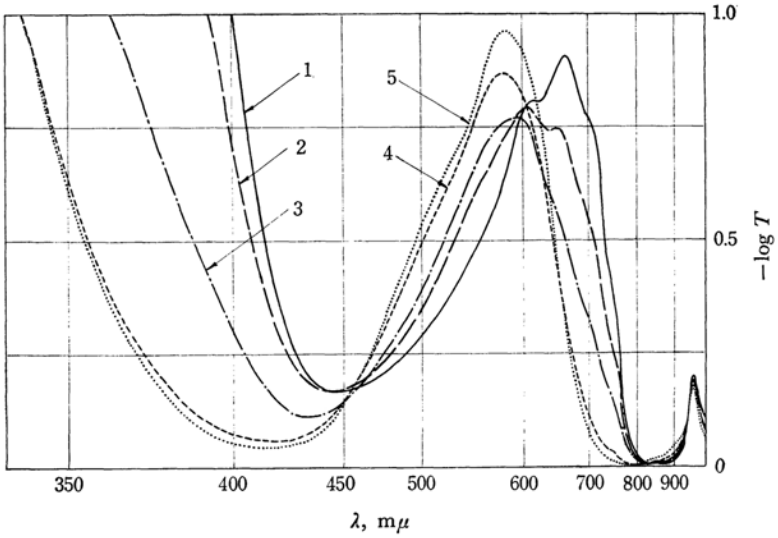

Fig. 2. The effect of potassium acetate on the absorption spectrum of cobalt(II) ion at 210°C.
The solution used are mixtures of CH_3OH (54 mol.%), AcOH (6.0 mol.%) and wates (40 mol.%) containing CoI_2 (0.10 mol.%), NaI (0.20 mol.%) and potassium acetate (0.0—0.30 mol.%). The added amounts of potassium acetate are (1) 0 mol.%, (2) 0.05 mol.%, (3) 0.10 mol.%, (4) 0.20 mol.%, (5) 0.30 mol.%

carbon monoxide - hydrogen*8 to form acetaldehyde, ethanol and acetic esters. As is shown in Table II, the addition of potassium acetate surely increase the methanol conversions into C_2-oxygenated compounds, especially into ethanol, but the reaction nearly stops when the amount of potassium acetate added becomes about three times as much as that of cobalt(II) ions.

These salts of carboxylic acids dissolve well in aqueous solutions and dissociate nearly completely, although the dissociation constants of their acid forms are small.*9 It is to be expected, therefore, that the addition of these salts results in a decrease in the concentration of hydrogen ions in the solutions, especially in the early period of the reactions mentioned above. This expectation is supported by the results obtained using borax, which is well known to make a good buffer solution. Hydrogen ions are considered to increase the reaction rates of dimethyl ether formation and the polymerizations of the acetaldehyde produced. The addition of suitable amounts of these salts, therefore, results in a decrease in the amount of dimethyl ether formed and an increase in the methanol conversions into C_2-oxygenated compounds, as is shown in Table I and II. However, it was very difficult to obtain more direct information regarding the behavior of hydrogen ions during the course of the reactions.*10

The Absorption Spectrum of Cobalt(II) Ions.—The cobalt(II) ion species is octahedral in aqueous solutions, while at an elevated temperature it is tetrahedral. The tetrahedral species of the $[CoX_4]^{2-}$ type, where X represents Cl^-, Br^-, I^-, AcO^-, NCS^-, etc., shows only one main absorption band in the visible region of the spectrum due to d'd electronic transitions. In glacial acetic acid, $[Co(AcO)_4]^{2-}$ has an absorption from 450 to 650 mμ, the maximum wavelength of which is 565 mμ, and the extinction coefficient of which is 1700 mol^{-1}. cm^{-1}; $[CoI_4]^{2-}$ has an absorption from 620 to 810 mμ, the maximum wavelength of which is 755 mμ, and the extinction coefficient of which is 1050 $mol.^{-1}$ cm^{-1}. When the temperature of the solution containing cobalt(II) ions, acetate ions and iodide ions is raised to 210°C, cobalt(II) ions form tetrahedral species of the $[Co(AcO)_{4-n}I_n]^{2-}$ (n=0—4) type and the addition of acetate shifts the visible absorption to shorter wavelength. Figure 2 shows the effect of potassium acetate on the absorption of cobalt(II) ions at 210°C in the absence of the reaction of methanol with carbon monoxide. On the other hand, cobalt carbonyls as $Co_2(CO)_8$ and $HCo(CO)_4$ have no absorption in the visible region because of their electronic configurations of

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*8 In this reaction, it is unnecessary to add water to methanol (See This Bulletin, **37**, 236 (1964)).

*9 10^{-4}—10^{-5} at 25°C. For example, the dissociation constants of acetic acid are 1.75×10^{-5} (25°C) and 1.54×10^{-5} (60°C); these constants are nearly independent of the concentrations.

*10 A preliminary experiment indicated that the amount of dimethyl ether formed increased upon an increase in the amount of sodium iodide added, while it decreased upon an increase in the amount of potassium acetate.

d^{10}, although they have very strong absorptions in the near ultraviolet region. Therefore, the visible absorption of cobalt(II) ions would disappear if most of cobalt(II) ions formed cobalt carbonyls in the course of the reaction. Figure 3 shows the absorption spectra in the course of the reaction of the acetic acid synthesis under the same conditions as those used in the experimental run of the curve 3 in Fig. 1, except that the special autoclave for taking absorption spectra could not be shaken so much. When small amounts of potassium acetate are present in the solution, the absorption from 500 to 650 mμ decreases and that in the longer wavelengths increases as soon as carbon monoxide has been introduced up to 300 kg./cm^2 at 210°C. However, the absorption from 500 to 600 mμ gradually increases as the reaction time goes on. This shows that the reaction is accompanied by an increase in the amount of tetrahedral iodo-cobalt(II) complex ions. However, all the absorptions from 500 to 700 mμ decrease when the amount of acetate added becomes large until they disappear nearly completely when 0.30 mol.% is added. In the near ultraviolet region, the strong absorptions always take place. These are considered to be partly due to the charge transfer from iodide ions to cobalt(II) ions and partly due to cobalt carbonyls, although it was very difficult to distinguish them from each other. The variation in the absorption spectra of Fig. 3 and the curve 3 in Fig. 1 shows that the amount of cobalt(II) ions present in the solution during the course of the reaction of methanol with carbon monoxide decreases with an increase in the amount of acetate added and that, when the reaction rate is promoted with this catalyst, most of the cobalt(II) ions do not form cobalt carbonyls, but tetrahedral complex ions of the $[Co(AcO)_{4-n}I_n]^{2-}$ type.

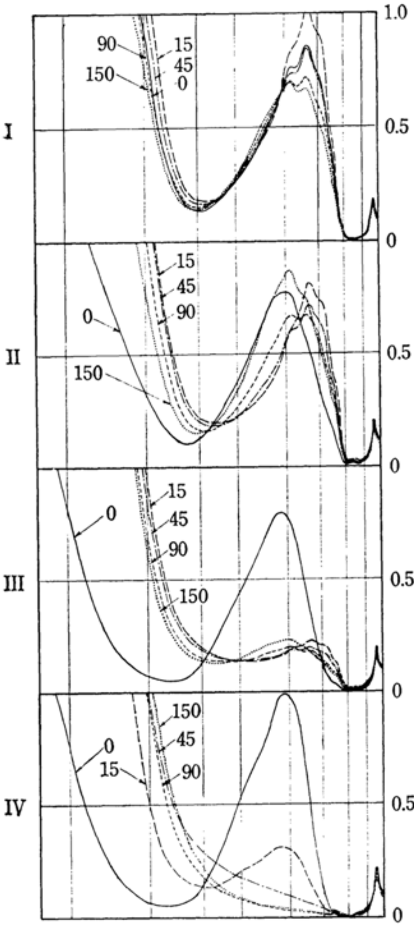

Fig. 3. The variation in the absorption spectrum of cobalt(II) ion in course of the reaction of the acetic acid synthesis under the constant pressure of 300 kg./cm^2 at 210°C.

The solution used are the same as these used in Fig. 2. and the added amounts of potassium acetate are I 0 mol.%, II 0.10 mol.%, III 0.20 mol.% and IV 0.30 mol.%. Numbers in the figure are the times (min.) since carbon monoxide has been introduced up to 300 kg./cm^2 at 210°C.

On the Reaction Mechanism.—Reppe estimated the course of the reaction to be as follows[1,5]:

$$3\,CoI_2 + 2\,H_2O + 10\,CO \rightarrow Co_2(CO)_8 + 4HI + 2\,CO_2$$

$$Co_2(CO)_8 + H_2O + CO \rightarrow 2\,HCo(CO)_4 + CO_2$$

$$CH_3OH + HI \rightarrow CH_3I + H_2O$$

$$CH_3I + HCo(CO)_4 \rightarrow CH_3Co(CO)_4 + HI$$

$$CH_3Co(CO)_4 \rightleftarrows CH_3COCo(CO)_3$$

$$CH_3COCo(CO)_3 + CO \rightarrow CH_3COCo(CO)_4$$

$$CH_3COCo(CO)_4 + H_2O \rightarrow HCo(CO)_4 + AcOH$$

The effect of acetate on methanol conversion into C_2-oxygenated compounds may be correlated with the concentration of hydrogen ions in the solution. The following explanation on the basis of Reppe's mechanism seems possible. The increase in the amount of acetate added will be favorable to the formation of cobalt carbonyls and will prevent the formation of dimethyl ether from methanol, however, it will be unfavorable to the formation of methyl iodide from methanol and hydroionic acid because of the decrease in the concentration of hydrogen ions in the solution. The reaction rate, therefore, reaches its maximum only when a suitable amount of acetate is added to the solution. However, his mechanism is obviously inconsistent

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[5] The abstract of Reppe's lecture given in Japan, April, 1965, or N. von Kutepow, W. Himmele and H. Hohenschutz, *Chem. Ingr.-Tech.*, **37**, 383 (1965).

with the fact that most of the cobalt(II) ions are tetrahedral species during the course of the reaction so long as the reaction rate is promoted by this catalyst. From the experimental results, it may be postulated that both the conversion of methanol into acetic acid and its rate decrease with the increase in the amount of cobalt carbonyls formed in the early period of the reaction. This suggests that the main course of the reaction may be represented as follows:

$$I^- + H^+ \rightleftarrows HI, \quad AcOH \rightleftarrows AcO^- + H^+$$

$$CH_3OH + HI \rightleftarrows CH_3I + H_2O$$

$$[Co(AcO)_{4-n}I_n]^{2-} + CO \rightarrow [(OC)Co(AcO)_{4-n}I_n]^{2-}$$

$$[(OC)Co(AcO)_{4-n}I_n]^{2-} + CH_3I \rightarrow [CH_3COCo(AcO)_{4-n}I_{n+1}]^{2-}$$

$$[CH_3COCo(AcO)_{4-n}I_{n+1}]^{2-} + HR \rightarrow [Co(AcO)_{3-n}I_{n+1}]^{2-} + CH_3COR + AcOH$$

$$(R\text{: } OCH_3, \text{ OH or H})$$

$$[Co(AcO)_{3-n}I_{n+1}]^{2-} + AcO^- \rightarrow [Co(AcO)_{4-n}I_n]^{2-} + I^-$$

Summary

We have examined the effects of the salts of carboxylic acids, especially acetates, on the reaction of methanol with carbon monoxide in the presence of a mixture of cobalt(II) ion and iodide ion ($I^-/Co^{2+}=4$) as a catalyst, and on the visible absorption spectra of cobalt(II) ions during the course of the reaction. Both the methanol conversions into C_2-oxygenated compounds and their reaction rates reach a maximum when the amounts of potassium acetate added are from one to two times as much as that of cobalt(II) ions. However, these reactions stop nearly completely when they become more than four times. The variation in the absorption spectrum of cobalt(II) ion in the course of the reaction shows that most of the cobalt(II) ions are tetrahedral species of the $[Co(AcO)_{4-n}I_n]^{2-}$ type so long as the reaction is promoted by the catalyst. From the experimental results and our discussion, it has been postulated that the increase in the amount of an acetate added is favorable to the formation of cobalt carbonyls and helps prevent methanol from forming dimethyl ether, while the reaction rate of methanol with carbon monoxide to form C^2-oxygenated compounds decreases with an increase in the amount of carbonyls formed in the early period of the reaction.