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Behavior of Methyl Iodide in the Reaction of Acetic Acid Synthesis from Methanol and Carbon Monoxide

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The reaction of methyl iodide with carbon monoxide in the presence of cobalt(II) iodide as the catalyst has been investigated to know the effect of methyl iodide on the acetic acid synthesis from methanol and carbon monoxide catalyzed by the same catalyst. The reaction, $CH_3I+CO+H_2O \rightarrow CH_3COOH+HI$, does not take place before the methyl iodide used has been hydrolyzed completely into methanol and sodium iodide by adding enough amount of sodium acetate ($CH_3I+CH_3COONa+H_2O \rightarrow CH_3OH+NaI+CH_3COOH$). Methyl iodide also strongly inhibits the reaction of methanol with carbon monoxide catalyzed by cobalt(II) ion or dicobalt octacarbonyl, although iodide ion promotes the reaction effectively. The promotion effect of iodide ion has been discussed by considering the effect of an additive on carbonylation reactions in terms of a labilizing ligand and a non-labilizing ligand and a possible reaction scheme of methanol with carbon monoxide catalyzed by cobalt(II) iodide has been proposed.

In the reaction of acetic acid synthesis from methanol and carbon monoxide in the presence of cobalt(II) iodide as the catalyst, hydrocobalt tetracarbonyl and methyl iodide were estimated to be formed in the course of the reaction as follows[1]: $2CoI_2+11CO+3H_2O \rightarrow 2HCo(CO)_4+4HI+3CO_2$, $HI+CH_3OH \rightarrow CH_3I+H_2O$. One may anticipate that the reaction of methyl iodide with carbon monoxide must be catalyzed more effectively by hydrocobalt tetracarbonyl to form acetic acid: $CH_3I+CO+H_2O \xrightarrow{HCo(CO)_4} CH_3COOH+HI$. This reaction, however, practically does not take place under the same conditions as those of the reaction with methanol. In our preceding papers dealing with the absorption spectrum of cobalt(II) ion in the course of the reaction of methanol with carbon monoxide, it was shown that most of cobalt(II) ion does not form dicobalt octacarbonyl, but tetrahedral iodo-cobalt(II) complex, $[Co(CH_3COO)_{4-n}I_n]^{2-}$,[2] and that the reaction is accelerated by adding a small amount of potassium acetate in spite that the presence of such a salt is unfavorable for the formation of methyl iodide from methanol and hydroiodic acid.[3] The addition of potassium acetate, in fact, effectively decomposes methyl iodide into methanol and potassium iodide through the reaction of $CH_3I+CH_3COOK+H_2O \rightarrow CH_3OH+CH_3COOH+KI$. It should be abandoned to discuss these facts in terms of the hydrocobalt tetracarbonyl and methyl iodide as the catalyst.

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[1] N. von Kutepow, W. Himmele and H. Hohenschutz, *Chem. Ingr. Tech.*, **37**, 383 (1965).

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

[3] T. Mizoroki and M. Nakayama, This Bulletin, **39**, 1477 (1966).

This work was undertaken to investigate the effect of methyl iodide on the reaction of methanol with carbon monoxide catalyzed by cobalt(II) iodide and to fully discuss the catalytic action of iodide ion and the course of the reaction.

Experimental

The apparatus and materials used in carrying out the reactions were the same as those described earlier.[3] The amounts of methanol, methyl acetate, dimethyl ether, methyl iodide and water were determined by the same gas chromatographic procedure described in the same paper. When the amount of methyl iodide contained in a liquid product was more than 0.1 mol% based on the methanol used (25% based on the cobalt(II) ion used), it was quantitatively determined by this gas chromatographic procedure.

Results

The Reaction of Methyl Iodide with Carbon Monoxide. Methyl iodide (0.40 mol), water (6.0 mol) and cobalt(II) iodide (0.004 mol) were placed in the autoclave (300 *ml* in vol) and carbon monoxide (40—50 kg/cm^2) was introduced at a room temperature. It had been heated up to 215°C and kept the temperature constant for about one hour before the carbon monoxide was introduced again up to 350 kg/cm^2. The reaction was carried out at the constant pressure for 2 hr. Under these conditions, practically no carbon monoxide was absorbed and the reaction of $CH_3I + CO + H_2O \rightarrow CH_3COOH + HI$ did not take place. After the reaction, 0.23 mol (58%) of methyl iodide used was hydrolyzed into methanol and hydroiodic acid. While a nearly calculated amount of carbon monoxide was absorbed on adding sodium acetate more than the equimolar amount of methyl iodide used ($CH_3COONa/CH_3I \geqq 1$) and 100% of methyl iodide used reacted with carbon monoxide to form acetic acid. The results are represented in Fig. 1 and Table 1. No carbon monoxide was absorbed as long as the amount of sodium acetate added was less than 0.40 mol $CH_3COONa/CH_3I < 1$). The hydrolysis of methyl iodide was checked by heating the solutions used in the experiments 3 and 6 without introducing any carbon monoxide. As shown in B3 and B6 of Table 1, 0.05 mol (13%) of methyl iodide used remained unchanged in the experiment B3 ($CH_3COONa/CH_3I = 0.75$), no methyl iodide, however, was detected in B6 ($CH_3COONa/CH_3I = 1.25$). These results show that the absorption of carbon monoxide takes place only when sodium acetate is added enough to hydrolyze the methyl iodide used completely and that the reaction can be represented as

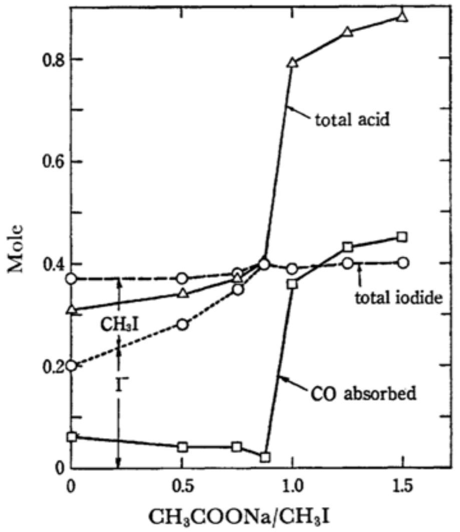

Fig. 1. Plots of the total acid formed and the carbon monoxide absorbed against the amounts of sodium acetate added.

TABLE 1. EFFECT OF ACETATE ON THE REACTION OF METHYL IODIDE WITH CARBON MONOXIDE

Exp. No.	CH_3COONa/CH_3I	Acid (mol)			I^- (mol)		
		Acid	CH_3COOCH_3	Total	CH_3I	I^-	Total
1	0.0	0.31	—	0.31**	0.17	0.20**	0.37
2	0.50	0.34	—	0.34	0.09	0.28	0.37
3	0.75	0.29	0.08	0.37	0.03	0.35	0.38
4	0.88	0.33	0.08	0.41	0.0	0.40	0.40
5	1.00	0.79	0.0	0.79	0.0	0.39	0.39
6	1.25	0.85	0.0	0.85	0.0	0.40	0.40
7	1.50	0.88	0.0	0.88	0.0	0.40	0.40
B3	0.75	0.27	0.08	0.35	0.05	0.34	0.39
B6	1.25	0.30	0.11	0.41	0.0	0.40	0.40
B*6′	1.25	0.83	0.0	0.83	0.0	0.40	0.40

* CH_3OH 0.4 mol, H_2O 5.6 mol, CH_3COOH 0.4 mol, CH_3COONa 0.1 mol, NaI 0.4 mol and CoI_2 0.004 mol.

** The difference in the amounts between total acid (0.31) and I^- (0.20) is probably caused by the formation of formic acid.

follows:

$$CH_3I + H_2O \rightarrow CH_3OH + HI \qquad (a)$$

$$HI + CH_3COONa \rightarrow CH_3COOH + NaI \qquad (b)$$

$$+ \quad CH_3OH + CO \rightarrow CH_3COOH \qquad (c)$$

$$CH_3I + CH_3COONa + CO + H_2O \rightarrow 2CH_3COOH + NaI \qquad (d)$$

The acids formed in the experiments 1—4 are the sum of the hydroiodic acid from (a) and the acetic acid from (b), they, however, do not contain the acetic acid formed from (c), because no carbon monoxide is absorbed. The experiment B6′ shown in Table 1 is the result obtained from the reaction of methanol with carbon monoxide under the same condition as that of the experiment 6 except that no methyl iodide was added to the starting materials. The absorption rates of carbon monoxide in the experiments 6 and B6′ are shown in Fig. 2. The amount of carbon monoxide absorbed in the experiment B6′ was nearly the same as that in the experiment 6 and negligibly small amounts of dimethyl ether and acetaldehyde were present in the product, but neither methanol, methyl acetate nor methyl iodide were detected. That the amount of the total acid is more than the calculated one (0.80 mol) is caused by the formation of a small amount of formic acid, because water was added enough to dissolve lots of sodium acetate or sodium iodide completely.

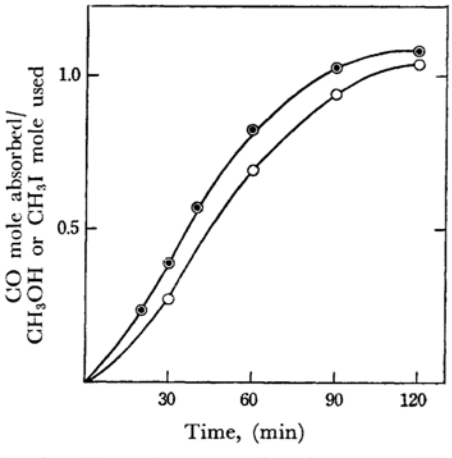

Fig. 2. Absorption rates of carbon monoxide.

⊙ the reaction with methyl iodide (No. 6)
○ the reaction with methanol (No. B6′)

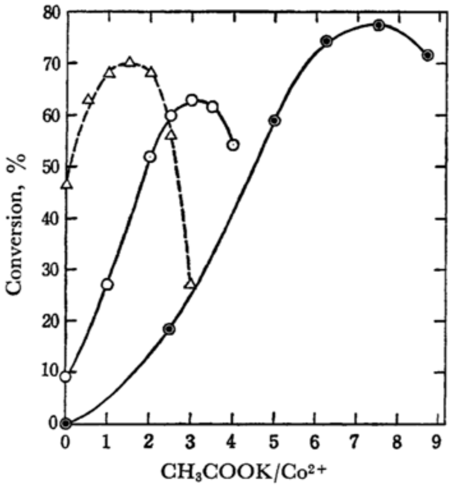

Fig. 3. Effect of methyl iodide on the reaction of methanol with carbon monoxide.

○ CH_3I 0.016 mol ⊙ CH_3I 0.040 mol
△ NaI 0.016 mol

Inhibition of Methyl Iodide in the Reaction of Methanol with Carbon Monoxide. Methanol (1.80 mol), acetic acid (0.20 mol), water (1.33 mol), cobalt(II) iodide (0.008 mol) and methyl iodide (0.016 mol, $CH_3I/CoI_2=2$ or 0.040 mol, $CH_3I/CoI_2=5$) were placed in the autoclave and the reaction with carbon monoxide was carried out for 2.5 hr under the constant pressure, 350 kg/cm^2 at the temperature, 215°C. Methyl iodide strongly inhibited the absorption rate of carbon monoxide and practically no acetic acid was formed especially when methyl iodide (0.040 mol) was added to the starting materials. While the inhibition was removed again by adding potassium acetate with which methyl iodide was hydrolyzed into methanol and potassium iodide. The result is shown in Fig. 3. The gas chromatographies of the liquid products obtained in the case of adding methyl iodide (0.016 mol) to the starting materials, showed that 0.003 mol of methyl iodide was contained in the product when the amount of potassium acetate added was 0.008 mol ($CH_3COOK/CH_3I=0.5$), while no methyl iodide was detected when it was more than 0.016 mole ($CH_3COOK/CH_3I \geqq 1$). For the purpose of investigating the effect of methyl iodide in the case of using dicobalt octacarbonyl as the catalyst, the following experiment was undertaken. Methanol (1.35 mol), acetic acid (0.15 mol), water (1.00 mol) and cobalt(II) acetate (0.006 mol) were placed in an autoclave (200 m*l*) equipped with another small high pressure vessel (25 m*l* in vol). Carbon monoxide was introduced up to the pressure, 300 kg/cm^2 at the temperature, 215°C and they were kept constant for about one hour to convert cobalt(II) acetate into dicobalt octacarbonyl,[*1] within which period no carbon monoxide was absorbed by the reaction with methanol. Then methyl iodide (0.003—0.024 mol in tetrahydrofuran) which had been

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[*1] To formation of $Co_2(CO)_8$ was checked by taking the absorption spectrum of cobalt(II) ion under the same condition. The visible absorption spectrum (from 450 to 700 mμ) of cobalt(II) ion disappears completely when it is converted into $Co_2(CO)_8$ or $[Co(CO)_4]^-$.

TABLE 2. MASS BALANCE OF THE LIQUID PRODUCT

Catalyst			Mass balance of methanol							Detected CH_3I
Inserted iodide		I/Co	Total CH_3COOH		Residual CH_3OH		$(CH_3)_2O$		Others	
Iodide	mmol		mol	%	mol	%	mol	%	%	mmol
CH_3I	3.0	0.50	0.50	37	0.56	41	0.21	16	6.1	0
	4.5	0.75	0.68	50	0.56	42	0.07	5.0	3.1	0
	6.0	1.00	0.63	47	0.49	36	0.12	9.2	8.0	0
	7.5	1.25	0.63	47	0.46	34	0.18	14	5.3	0
	12.0	2.00	0.52	38	0.46	34	0.23	17	10.4	3.8
	18.0	3.00	0.47	35	0.47	35	0.30	22	9.9	6.8
	24.0	4.00	0.28	21	0.44	32	0.35	26	21.1	8.3
HI	6.0	1.00	0.71	53	0.44	32	0.09	6.4	8.7	0
	18.0	3.00	0.50	37	0.40	29	0.24	18	15	3.8
NaI	6.0	1.0	0.48	36	0.82	61	0.01	1.0	2.1	0
	24.0	4.0	0.79	59	0.52	38	0.02	1.8	1.2	0
	36.0	6.0	0.91	67	0.37	27	0.03	2.5	2.9	0
	60.0	10.0	0.97	72	0.33	25	0.03	2.1	1.3	0

CH_3OH 1.35 mol, CH_3COOH 0.15 mol, H_2O 1.00 mol, $Co(CH_3COO)_2 \cdot 4H_2O$ 6.0 mmol.

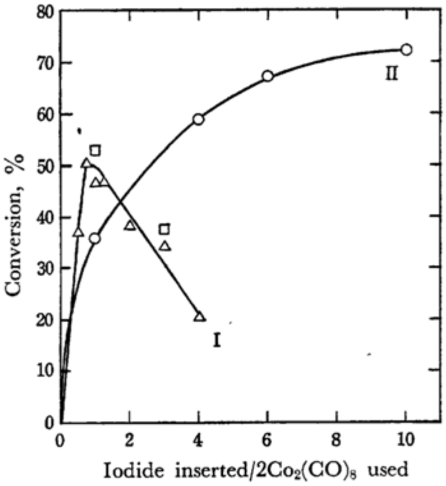

Fig. 4. Effect of iodide on the reaction of methanol with carbon monoxide in the presence of $Co_2(CO)_8$ as the catalyst.

△ CH_3I □ HI ○ NaI

charged in the small vessel was introduced into the autoclave by using a higher pressure of carbon monoxide and the reaction was carried out under the constant pressure, 350 kg/cm² for 2.5 hr. Mass balances of the liquid products are shown in Table 2 and methanol conversion (%) into total acetic acid (free acetic acid+methyl acetate) are plotted against the amount of methyl iodide introduced ($CH_3I/2Co_2(CO)_8$) in Fig. 4 (curve I). When the amount of methyl iodide introduced is 0.0045 mol ($CH_3I/2Co_2(CO)_8 \fallingdotseq 0.8$), methanol conversion becomes maximum and no methyl iodide was detected in the liquid product, the conversion, however, decreases sharply with increasing the amount of methyl iodide and that of dimethyl ether contained in the liquid products gradually increases. The same result is obtained on introducing hydroiodic acid*2 aqueous solution in place of methyl iodide. But it is very different from these results that the methanol conversion increases with increasing the amount of sodium iodide aqueous solution*2 introduced as shown by the curve II in Fig. 4.

Discussion

The following facts are, no doubt, inconsistent with the reaction scheme proposed by Reppe.1)
(i) When sodium iodide is used in place of methyl iodide or hydroiodic acid, the reaction rate of methanol with carbon monoxide increases with increasing the amount of sodium iodide added.
(ii) No methyl iodide is detected in the liquid product when the reaction rate is large enough.
(iii) In the course of the reaction, most of cobalt(II) ion does not form dicobalt octacarbonyl, but tetrahedral iodocobalt complex $[Co(CH_3COO)_{4-n}I_n]^{2-}$. The addition of sodium iodide or an acetate is unfavorable for the formation of methyl iodide, because the equilibrium constant of Eq. (e) is much smaller than that of Eq. (f).*3

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*2 The total amount of water added was constant in this experimental run (1.00 mol).

*3 The equilibrium constants, $\log K_p$ at 200°C, calculated from $\log K_p = -\Delta H^\circ_{298}/4.575T + \Delta S^\circ_{298}/4.575$ are -0.67 in Eq. (e) and 5.07 in Eq. (f), in which the entropy of CH_3COONa (39.2 cal/mol·°K) is obtained from assuming no change in the entropy of the reaction $CH_3COOH(g) + NaOH(s) \rightarrow CH_3COONa(s) + H_2O(g)$.

$$\mathrm{CH_3OH(g) + NaI(s) + CH_3COOH(g) \rightleftarrows CH_3I(g) + CH_3COONa(s) + H_2O(g) + 0.56\ kcal/mol} \tag{e}$$

$$\mathrm{CH_3OH(g) + HI(g) \rightleftarrows CH_3I(g) + H_2O(g) + 11.0\ kcal/mol} \tag{f}$$

The reaction rate, therefore, would not be increased by adding sodium iodide in place of methyl iodide or hydroiodic acid, if the formation of methyl iodide were necessary in the course of the reaction. If no detection of methyl iodide in the liquid product were caused by that the formation of methyl iodide were the rate determining step, the rate of the reaction with carbon monoxide would not depend on the pressure of carbon monoxide, nor the amount of cobalt(II) ion added. But, in fact, the higher the reaction pressure, the larger the reaction rate.[3,4]

Promotion Effect of Iodide Ion. Before the catalytic action of iodide ion will be discussed, it must be noticed that in a hydroformylation or a hydroesterification reaction catalyzed by $\mathrm{Co_2(CO)_8}$ or $\mathrm{Rh_2(CO)_8}$, its reaction rate is increased by adding an organic base such as pyridine[5-7] or *N*-ethylpyrolidine,[6] it is, however, rather strongly inhibited by carbon monoxide[5] or phosphorous compounds[6] such as $\mathrm{P(C_6H_5)_3}$ or $\mathrm{P(OC_2H_5)_3}$. In his recent paper,[8] Matsuda explained that in the hydroesterification of propylene or acrylonitrile pyridine (Py) would accelerate the insertion step of carbon monoxide to form acylcobalt tricarbonyl represented by $\mathrm{C_3H_7Co(CO)_4 + Py \rightarrow C_3H_7COCo(CO)_3Py}$ or $\mathrm{NCC_2H_4Co(CO)_4 + Py \rightarrow NCC_2H_4COCo(CO)_3Py}$. Such insertion reactions are well known also in the reactions of $\mathrm{RCo(CO)_4}$ with carbon monoxide or phosphorous compounds[9] and of $\mathrm{CH_3Mn(CO)_5}$ with carbon monoxide,[10] phosphorous compounds, amines[11] or iodide ion.[12] The question is why neither phosphorous compounds nor carbon monoxide accelerate the carbonylation reactions. According to the classification of ligands defined recently by Angelici,[13] halogen ions amines are labilizing ligands (hard base*[4]), while carbon monoxide and phosphorous compounds are non-labilizing ligands (soft base*[4]). This classification may provide a possible explanation on the effect of an additive on the carbonylation reactions catalyzed by a cobalt carbonyl. The following reaction scheme has been reported as a reasonable one of an oxo-reaction.[9] Although kinetic data have not been found enough, the rate determining step is probably the reaction (iii) in a hydroformilation reaction, while in a hydroesterification reaction it would be the reaction (ii).

$$\mathrm{RCHCH_2 + HCo(CO)_4 \rightleftarrows RC_2H_4Co(CO)_4} \tag{i}$$

$$\mathrm{RC_2H_4Co(CO)_4 \rightleftarrows RC_2H_4COCo(CO)_3} \underset{-\mathrm{CO}}{\overset{+\mathrm{CO}}{\rightleftarrows}} \mathrm{RC_2H_4COCo(CO)_4} \tag{ii}$$

$$\mathrm{RC_2H_4COCo(CO)_3 + HR \rightleftarrows RC_2H_4COR + HCo(CO)_3} \tag{iii}$$

$$\mathrm{HCo(CO)_3 + CO \rightleftarrows HCo(CO)_4} \tag{iv}$$

$$(\mathrm{R{=}H\ or\ OCH_3})$$

The effect of an additive in this scheme, can be explained by considering Eq. (ii′). When L is one of labilizing ligands (Py, halide ion, some

$$\mathrm{RC_2H_4Co(CO)_4 + L \rightleftarrows RC_2H_4COCo(CO)_3L} \tag{ii′}$$

solvent), acylcobalt tricarbonyl will become sufficiently reactive, the rate determining step, then, will be the reaction (ii′). On the other hand, when L is one of non-labilizing ligands (carbon monoxide or phosphorous compounds), acylcobalt tricarbonyl will become unreactive, the rate determining step, then, will be the reaction (iii).

In the reaction of methanol with carbon monoxide, authors postulated $[\mathrm{Co(CO)I}_n\mathrm{(CH_3COO)}_{4-n}]^{2-}$ and $[\mathrm{Co(OCCH_3)I}_n\mathrm{(CH_3COO)}_{4-n}]^{2-}$ (n=1—4) as its intermediates.[3] Booth and Chatt[14] reported that $[\mathrm{CoX_2(PEt_3)_2}]$ ($\mathrm{Et{=}C_2H_5}$, $\mathrm{X{=}Cl^-}$, $\mathrm{Br^-}$ or $\mathrm{I^-}$) reacts with carbon monoxide at a room temperature under an atmospheric pressure to form penta-coordinating and paramagnetic carbonyl complexes $[\mathrm{CoX_2(CO)(PEt_3)_2}]$. The order of their stabilities is $\mathrm{I^- > Br^- > Cl^-}$. It would be explained from π-bonding theory that the coordination of carbon monoxide to cobalt(II) ion is facilitated by adding a good donors, as iodide ion, capable of coordinating to the metal ion. They also isolated the acyl complexes, *trans*-$[\mathrm{MX(COR)(PEt_3)_2}]$ (M=Pd or Pt, R=alkyl or aryl) from

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4) T. Mizoroki, M. Nakayama, Y. Ando and M. Furumi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **65**, 1049 (1962).

5) I. Wender, H. W. Sternberg and M. Orchin, "Catalysis," Vol. V, ed. by P. H. Emmett, Reinhold Pub. Co., New York (1957), p. 110.

6) J. Falbe and N. Huppes, *Brenn. Chem.*, **48**, 46 (1967).

7) A. Matsuda and H. Uchida, This Bulletin, **38**, 710 (1965).

8) A. Matsuda, *ibid.*, **40**, 135 (1967).

9) R. F. Heck, "Advan. Organomet. Chem.," Vol. IV, ed. by F. G. Stone and R. West, Academic Press, New York (1966), p. 242.

10) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 30 (1962).

11) R. J. Mawby, F. Basolo and R. Pearson, *J. Am. Chem. Soc.*, **80**, 3994 (1964).

12) F. Calderazzo and K. Noack, *J. Organomet. Chem.*, **4**, 250 (1965).

13) R. J. Angelici and J. R. Graham, *Inorg. Chem.*, **6**, 988 (1967).

*4 It can be said, labilizing ligands have no empty π orbital and they are good σ donors, while non-labilizing ligands have empty π orbitals (good dπ acceptor), although this classification can not be understood in terms of π-bonding theory.

14) G. Booth and J. Chatt, *J. Chem. Soc.*, **1962**, 2099.

trans-$[MXR(PEt_3)_2]$ and carbon monoxide[15] and estimated that such complexes would be intermediates in carbonylation reactions, although such cobalt or nickel complexes were too unstable to be isolated.

Inhibition Effect of Hydroiodic Acid. It can not be understood well why both methyl iodide and hydroiodic acid inhibit the reaction of methanol with carbon monoxide. The following facts, however, may provide an explanation on their inhibition effects. The addition of a salts of weak acid (acetate, benzoate, borax *etc*) is very effective for the formation of dicobalt octacarbonyl from cobalt(II) iodide, although it is easily formed under a milder condition without adding any additive when a cobalt(II) salt of weak acid (acetate or carbonate) is used as the starting material. Weak acids salts are good acceptors of hydroiodic acid formed, which results in decreasing the hydrogen ion concentration, because hydroiodic acid is a much stronger acid. This suggests that proton, which is an acceptor of electron, probably inhibits the coordination of carbon monoxide to cobalt(II) ion. On the other hand, Wakamatsu confirmed that the treatment of $RMn(CO)_5$ ($R=CH_3$–, C_6H_5– or $C_6H_5CH_2$–) with hydroiodic acid resulted in forming nearly stoichiometric amounts of RH and $IMn(CO)_5$ against his expectation that RI and $HMn(CO)_5$ would have been formed.[16] The similar reaction would take place between $CH_3Co(CO)_4$ and HI.

A Possible Reaction Scheme. From the above discussion, the course of the reaction of methanol with carbon monoxide catalyzed by cobalt(II) iodide can be represented as follows:

$$\text{Co(II)} + \text{CO} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{Co(II)–CO} \tag{v}$$

$$H_2O \overset{K_1}{\rightleftarrows} H^+ + OH^-,$$

$$CH_3OH + H^+ \overset{K_2}{\rightleftarrows} CH_3OH_2{}^+ \tag{vi}$$

$$CH_3OH_2{}^+ + \text{Co(II)–CO} \overset{K_3}{\rightleftarrows} CH_3\text{–Co(II)–CO} + H_2O \tag{vii}$$

$$CH_3\text{–Co(II)–CO} + I^- \xrightarrow{k_3} CH_3CO\text{–Co(II)–I} \tag{viii}$$

$$CH_3CO\text{–Co(II)–I} + HR \xrightarrow{\text{fast}} CH_3COR + \text{Co(II)} + H^+ + I^- \tag{ix}$$

(where R is H, OH or OCH_3 and Co(II) represents $[Co(CH_3COO)_{4-n}I_n]^{2-}$)

The formation of carbonium ion from methanol (Eq. (vi)) is generally accepted in the course of the esterification or dehydration of methanol catalyzed by hydrogen ion. In this scheme, it is postulated that the breaking of the bond between carbon and oxygen of methanol is assisted by hydrogen ion and that the formation of an acyl complex is promoted by iodide ion (Eq. (viii)). On the assumption that the reactions (vi) and (vii) become equilibrium and that the concentration of Co(II)–CO is nearly constant during the reaction, one can derive the following equations, which is qualitatively consistent with the reported results[3,4] obtained from the absorption rate of carbon monoxide.

$$r = k_3[CH_3Co(II)CO][I^-]$$

$$= \frac{k_1k_3K_1K_2K_3[Co(II)][I^-][p_{CO}][CH_3OH]}{k_2[OH^-]+k_3K_1K_2K_3[CH_3OH][I^-]}$$

$$k_2 \gg k_3K_1K_2K_3$$

$$r = \frac{k_1k_3K_1K_2K_3}{k_2[OH^-]}[Co(II)][p_{CO}][I^-][CH_3OH]$$

$$= \frac{k_1k_3K_2K_3}{k_2[H_2O]}[Co(II)][I^-][p_{CO}][H^+][CH_3OH]$$

From this reaction scheme, the effect of acetate shown in Fig. 3 can be also explained: the addition of potassium acetate will decrease the concentration of $[H^+]$ which would inhibit the coordination of carbon monoxide to cobalt(II) ion, so k_2 will become smaller and r increases, while the decrease in $[H^+]$ must be unfavorable for the equilibrium concentration of $[CH_3OH_2{}^+]$, r is, then, decreased again by adding excess amounts of acetate.

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[15] G. Booth and J. Chatt, *Proc. Chem. Soc.*, **1961**, 67.

[16] H. Wakamatsu and K. Sakamaki, Preprints for the 20th Annual Meeting of the Chemical Society of Japan, (April, 1967), Part III, p. 587.