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The Cobalt Carbonyl-catalyzed Hydroesterification of Acrylonitrile with Carbon Monoxide and Methanol in the Presence of a Small Amount of Hydrogen and a Limited Amount of Pyridine

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The present reaction was studied in connection with our preceding research on the hydroesterification of propylene (This Bulletin, **38**, 710 (1965)). The cobalt carbonyl-catalyzed reaction was successfully carried out in the presence of a small amount of hydrogen and a limited amount of pyridine; methyl esters of α- and β-cyanopropionic acids were thus obtained, the former in a larger amount than the latter. As the temperature decreased or as the partial pressure of carbon monoxide increased, the selectivity of the reaction toward the methyl α-cyanopropionate grew larger. The reaction mechanism was mainly investigated by kinetic methods. The infrared spectra of the catalyst solutions were measured at -60°C with a low-temperature cell. It was found by the IR study that acylcobalt carbonyls were formed in the acrylonitrile solution of dicobalt octacarbonyl and pyridine when it was treated under the same conditions (temperature and pressure) as in the reaction. It was found from the results of kinetic studies that the mechanisms of reactions at temperatures above and below 100°C were different; each of these mechanisms was discussed.

In a preceding paper on the hydroesterification of propylene with carbon monoxide and methanol in the presence of dicobalt octacarbonyl,[1] it was reported that the reaction was promoted by the addition of a small amount of hydrogen and excess pyridine, and that the reaction in their presence was first-order in propylene, but that the reaction in their absence was zero-order in propylene, as was mentioned in the study by Ercoli *et al.*, who investigated the hydroesterification of cyclohexene with pure carbon monoxide and methanol.[2]

The first object of the present investigation was to explore the possibility of using this method to promote a reaction of acrylonitrile (AN) with carbon monoxide and methanol, thus obtaining methyl esters of α- and/or β-cyanopropionic acid, which may be useful in industry. For example, methyl α-cyanopropionate can be converted by the reaction with acrylonitrile into α-methyl-α-carbomethoxyglutaronitrile, which can then be hydrolyzed and decarboxylated into α-methylglutaric acid,[3] while methyl β-cyanopropionate can be hydrogenated over a nickel catalyst to give pyrrolidone.[4]

The other object of this investigation was to obtain information on the mechanism of this cobalt carbonyl-catalyzed reaction in the presence of a small amount of hydrogen and a limited amount of pyridine.

Experimental

Reagents such as acrylonitrile (AN), methanol, and pyridine (Py) were obtained commercially and rectified before use. The hydroesterification reactions were carried out in the same 300 cc stainless-steel autoclave which has been described previously.[1] After AN, methanol, Py and dicobalt octacarbonyl ($Co_2(CO)_8$) had been put into the autoclave,[5] the air inside it was replaced by carbon monoxide with a fixed content of hydrogen and it was brought to the desired reaction temperature and pressure by the additional charging of the same gas under heating. Then the stirrer was begun; the reaction took place after a short induction time. The total pressure was kept constant during the reaction by supplying carbon monoxide with a fixed content of hydrogen from a 500 cc-pressure storage vessel through a pressure regulator, while the reaction temperature was controlled within a range of ±1°C. The hydrogen content of the supplied gas was adjusted so as to keep the hydrogen partial pressure during the reaction nearly constant. The amount of gas supplied during the reaction was calculated from the pressure drop in the pressure storage. After a reaction period of an hour, the autoclave was cooled and the composition of the remaining gas was determined by the usual absorption method, while the liquid product was weighed and analyzed by gas chromatography. Quantitative analyses by the gas chromatographical method were performed by adding ethylbenzene as an internal standard to the

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[1] A. Matsuda and H. Uchida, This Bulletin, **38**, 710 (1965).

[2] R. Ercoli, M. Avanzi and G. Moretti, *Chim. Ind.* (*Milan*), **37**, 865 (1955).

[3] M. F. Ansel and D. H. Hey, *J. Chem. Soc.*, **1950**, 1683.

[4] C. F. Winans and H. Adkins, *J. Am. Chem. Soc.*, **55**, 4167 (1933).

[5] $Co_2(CO)_8$ was put in a stainless-steel saucer and placed upon a wing of the stirrer, so that it fell into the solution as soon as the stirrer began to move.

reaction product at the temperature of 150°C with a 3 m column of cellite plus a ethyleneglycol - adipic acid polyester.

For the measurement of the infrared spectra of various samples and for the determination of the ratio of the combined carbon monoxide (mole) to cobalt (g atom) (hereafter denoted by CO_c/Co) in the reacting solution, experiments at a similar reagent concentration were carried out simultaneously in another 100 cc autoclave. The inner wall of the autoclave was lined with titanium lest the liquid samples be contaminated by corrosion of the autoclave material. Solutions of cobalt carbonyl were kept being stirred under definite conditions in the autoclave, and at definite times aliquot samples of these solutions were quickly withdrawn through a titanium dip tube into a receiver cooled in dry ice - methanol. The infrared spectra of these aliquot samples were measured at -60°C in a low-temperature cell. The Co_c/Co ratio was determined as follows. After nitrogen of a high purity had been bubbled through the dry ice-cooled aliquot sample to purge the dissolved carbon monoxide, the sample was poured into dilute sulfuric acid and heated to 90°C to decompose the whole cobalt carbonyls; the gas thus liberated was measured in volume and analyzed for carbon monoxide by the absorption method, while the amount of cobalt ions remaining in the solution was determined by the chelate titration method with EDTA.

Product Identification. The products were separated by distillation with a rectifier of the spinning-band type and identified by elemental analyses, infrared spectra, NMR spectra at 60 Mc (in carbon tetrachloride with tetramethylsilane as an internal standard), etc.

Methyl α-cyanopropionate: bp 74°C/10 mmHg. IR spectrum: C=O (ester) 1757 cm^{-1}. NMR spectrum: β-CH_3 τ 8.46 (doublet), α-CH τ 6.46 (quartet), OCH_3 τ 6.23 (singlet).

Found: C, 52.60; H, 6.00; N, 11.92%. Calcd for $C_5H_7NO_2$: C, 53.09; H, 6.24; N, 12.38%.
The structure of this compound was further confirmed by its hydrolysis to methylmalonic acid.

Methyl β-cyanopropionate: bp 96°C/10 mmHg. IR spectrum: C=O (ester) 1744 cm^{-1}. NMR spectrum: α-, β-CH_2 τ 7.36 (singlet), OCH_3 τ 6.28 (singlet).

Found: C, 52.78; H, 6.11; N, 12.08%. Calcd for $C_5H_7NO_2$: C, 53.09; H, 6.24; N, 12.38%.
The structure of this compound was further confirmed by its hydrolysis to succinic acid.

β-Cyanopropionaldehyde dimethyl acetal: bp 86°C/10 mmHg.
IR spectrum: C–O (acetal) 1065, 1083 cm^{-1}. NMR spectrum: α–CH_2 τ 8.08 (triplet), β–CH_2 τ 7.65 (triplet), OCH_3 τ 6.69 (singlet), CH τ 5.64 (triplet).

Found: C, 55.86; H, 8.08; N, 10.79%. Calcd for $C_6H_{11}NO_2$: C, 55.79; H, 8.58; N, 10.85%.

Results

The Effect of Pyridine on the Hydroesterification of AN. In the preceding research on the hydroesterification of propylene, it was revealed that pyridine (Py) was the most effective promoter of the reaction.(1) In connection with this previous finding, the effect of Py addition on the present reaction was first tested. As a result, it was found that the addition of Py was very effective, and that the reaction carried out in the presence of a small amount of hydrogen proceeded rapidly even at temperatures below 100°C in the presence of as little Py as 1—4 in terms of the $Py/Co_2(CO)_8$ mole ratio, resulting in a high yield of methyl cyanopropionate in a 1-hr reaction. It was found, however, that in the absence of Py the reaction proceeded very little. The reaction product was mainly composed of methyl esters of α- and β-cyanopropionic acids (α-, β-MCP), the former being larger in amount than the latter. The predominance of the α-cyano isomer is in contrast to the case of the hydroformylation of AN, where the β-cyano isomer is selectively produced, according to the literature.(6)

In the present hydroesterification runs the hydroformylation and the hydrogenation of AN also occured as side-reactions as a result of the presence of hydrogen, and β-cyanopropionaldehyde dimethyl acetal and propionitrile were produced in minor amounts respectively. Table 1 summarizes the results of the hydroesterification runs in the presence of varying amounts of Py at various temperatures. At reaction temperatures below 100°C the yields of the esters increase with the amount of Py; they reach a maximum when the $Py/Co_2(CO)_8$ mole ratio is 2 and then decrease. On the other hand, at reaction temperatures above 100°C they continue increasing with the amount of Py in the range of the present experiments. The α-MCP/β-MCP ratio increases with the amount of Py addition till the $Py/Co_2(CO)_8$ mole ratio reaches 3, but it tapers off thereafter. As the reaction temperature is lowered, keeping the $Py/Co_2(CO)_8$ ratio constant, the α-MCP/β-MCP ratio increases.

For the calculation of the reaction rate, the relation between the amount of reacted AN and that of the gas supplied during the reaction must be known, but the former can not simply be equated with the latter, because the hydroformylation of AN occurs as a side-reaction which consumes two moles of gas, *i. e.,* one mole of carbon monoxide and one mole of hydrogen, per mole of AN. To obtain information on the rates of side-reactions, Experiments Nos. 18 and 19, in which the yields of by-products are relatively large, were repeated, and aliquots (each *ca.* 1 cc) were withdrawn from the autoclave at several reaction times and analyzed. The results of the analyses are plotted against the reaction time in Fig. 1. As is shown in the figure, the amount of β-cyanopropionaldehyde dimethyl acetal increases almost linearly with the reaction

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6) J. Kato, H. Wakamatsu, R. Iwanaga and T. Yoshida, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **64**, 2139 (1961).

TABLE 1. THE EFFECT OF Py ON THE YIELDS OF PRODUCTS AT VARIOUS TEMPERATURES
4 mmol $Co_2(CO)_8$, 0.5 mol AN, 2 mol methanol; total pressure, 190 kg/cm^2; reaction period, 1.0 hr; hydrogen content of the carbon monoxide, 5.0%

Expt. No.	Reaction temp. °C	Added Py mmol	Amounts of products, mol[a)					α/β[b)
			AN	α-MCP	β-MCP	β-CPA	PN	
1	84	0	0.438	0.008	0.008	0.002	0	1.0
2	84	4	0.157	0.300	0.034	0.003	0.006	8.8
3	84	8	0.130	0.319	0.031	0	0.002	10.3
4	84	12	0.196	0.278	0.017	0	0.002	16.4
5	84	16	0.296	0.163	0.012	0	0	13.6
6	94	0	0.430	0.019	0.014	0.005	0.004	1.4
7	94	4	0.061	0.347	0.070	0.015	0.007	5.0
8	94	8	0.014	0.410	0.056	0.007	0.004	7.3
9	94	12	0.039	0.392	0.039	0	0.004	10.0
10	94	16	0.063	0.394	0.036	0	0.002	10.9
11	104	0	0.420	0.017	0.016	0.012	0.003	1.1
12	104	4	0.005	0.338	0.103	0.029	0.005	3.3
13	104	8	0.001	0·371	0.089	0.018	0.004	4.2
14	104	12	0.007	0.376	0.073	0.008	0.003	5.2
15	104	16	0.014	0.407	0.072	0.003	0.003	5.7
16	114	0	0.402	0.016	0.015	0.012	0.005	1.1
17	114	4	0	0.315	0.114	0.054	0.005	2.8
18	114	8	0	0.342	0.110	0.033	0.005	3.1
19	114	12	0	0.366	0.105	0.016	0.004	3.5
20	114	16	0.005	0.382	0.089	0.011	0.004	4.3
21	124	0	0.419	0.004	0.004	0.006	0.006	1.0
22	124	4	0.001	0.281	0.131	0.031	0.013	2.1
23	124	8	0.001	0.299	0.124	0.023	0.010	2.4
24	124	12	0	0.314	0.126	0.019	0.010	2.5
25	124	16	0.001	0.334	0.140	0.015	0.010	2.4

a) Abbreviations α-, β-MCP, β-CPA and PN stand for methyl α-, β-cyanopropionate, β-cyanopropionaldehyde dimethyl acetal and propionitrile.
b) α/β stands for the mole ratio α-MCP/β-MCP.

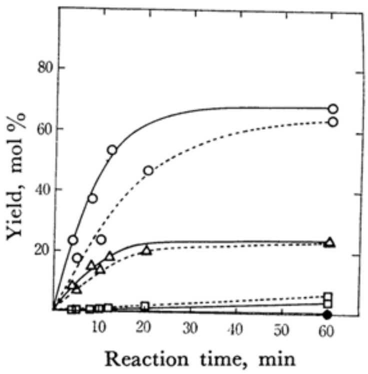

Fig. 1. The products yields (mol %) based on AN as functions of reaction time.
Full line: Expt. No. 19
Dotted line: Expt. No. 18
○ Methyl α-cyanopropionate
△ Methyl β-cyanopropionate
□ β-Cyanopropionaldehyde dimethyl acetal
● Propionitrile

time. As AN is converted by the overall reaction into MCP,[7) β-cyanopropionaldehyde dimethyl acetal, and propionitrile, the initial amount of AN (C_0 mole) can be equated with the sum total of the amounts at the reaction times, t, of AN (C_t mole), MCP (C_{et} mole), β-cyanopropionaldehyde dimethyl acetal (C_{ft} mole), and propionitrile (C_{ht} mole). Since C_0 is equal to 0.5, Eq. (1) follows:

$$0.5 = C_t + C_{et} + C_{ft} + C_{ht} \tag{1}$$

The amount of gas supplied during the reaction time t (V_t) is equal to the sum of C_{et}, $2C_{ft}$ and C_{ht}:

$$V_t = C_{et} + 2C_{ft} + C_{ht} \tag{2}$$

Hence, the amount of AN at the reaction time t (C_t) can be expressed as follows:

$$C_t = 0.5 - V_t + C_{ft} \tag{3}$$

[7) MCP represents both isomers of methyl cyanopropionate when put toghther.

TABLE 2. THE EFFECT OF TOTAL PRESSURE ON THE YIELDS OF PRODUCTS AT VARIOUS TEMPERATURES
4 mmol $Co_2(CO)_8$, 12 mmol Py, 0.5 mol AN, 2 mol methanol;
reaction period, 1.0 hr; hydrogen content of the carbon monoxide, 5.0%

Expt. No.	Reaction temp. °C	Pressure kg/cm²	Amounts of products, mol					α/β
			AN	α-MCP	β-MCP	β-CPA	PN	
26	84	60	0.441	0.042	0.010	0	0	4.2
27	84	90	0.273	0.196	0.023	0	0	8.5
28	84	120	0.165	0.292	0.031	0	0.003	9.4
29	84	150	0.178	0.295	0.019	0	0.003	15.5
30	104	60	0.249	0.094	0.047	0	0.005	2.0
31	104	90	0.033	0.320	0.125	0.003	0.010	2.6
32	104	120	0.007	0.357	0.113	0.006	0.008	3.2
33	104	150	0.003	0.373	0.098	0.007	0.009	3.8
34	124	60[a]	—	—	—	—	—	—
35	124	90	0.133	0.134	0.083	0	0.021	1.6
36	124	120	0.003	0.309	0.147	0.013	0.018	2.1
37	124	150	0.001	0.305	0.141	0.014	0.013	2.2

a) In experiment No. 34 no reaction occured.

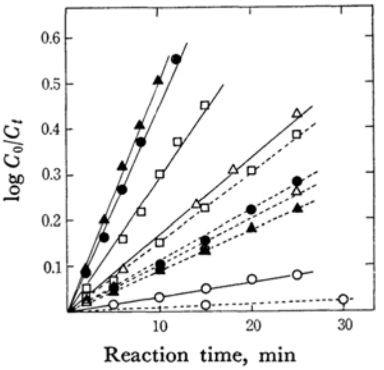

Fig. 2. The plot of log C_0/C_t *vs.* reaction time.
Full lines: The reactions carried out at 114°C
Dotted lines: The reactions carried out at 94°C
The mole ratio $Py/Co_2(CO)_8$ 0 1 2 3 4
Mark ○ △ □ ● ▲

Here, C_{ft}, the amount of β-cyanopropionaldehyde dimethyl acetal at the reaction time, *t*, can be calculated from the analytical value after a 1 hr reaction, since it is proportional to the reaction time, as is shown in Fig. 1.

Then $\log C_0/C_t$ was plotted against *t* in the earlier stages of the reaction; examples are shown in Fig. 2. The first-order reaction rate constant, *k*, was calculated from the inclination of the plotted line according to the equation:

$$k = (1/t) \ln C_0/C_t (\text{min}^{-1}) \qquad (4)$$

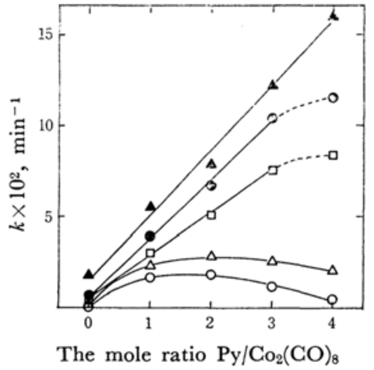

Fig. 3. The rate constant *k* plotted against the mole ratio $Py/Co_2(CO)_8$.
Reaction temperature °C 84 94 104 114 124
Mark ○ △ □ ● ▲

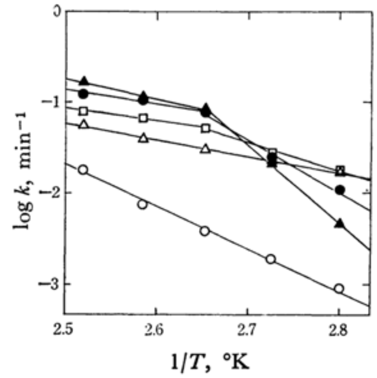

Fig. 4. Arrhenius plots of the rate constants *k*.
The mole ratio $Py/Co_2(CO)_8$ 0 1 2 3 4
Mark ○ △ □ ● ▲

The plot of *k* against the $Py/Co_2(CO)_8$ mole ratio at various temperatures is shown in Fig. 3. At reaction temperatures above 100°C, *k* increases linearly with the $Py/Co_2(CO)_8$ ratio except for final two points, *i. e.*, the experiments at 104 and 114°C when $Py/Co_2(CO)_8$ is 4, but at reaction temperatures below 100°C, *k* reaches a maximum when this ratio is 2, thereafter decreasing slowly. Arrhenius plots of *k* for various series of runs which were carried out with a fixed mole ratio, $Py/Co_2(CO)_8$, are shown in Fig. 4. The plotted lines are straight when the $Py/Co_2(CO)_8$ ratios are 0 or 1, but they bend downwards at about 100°C when the above ratios are 2, 3 or 4; this suggests that a change in the mechanism occurs at about 100°C.

The Effect of the Total Pressure. The effect of the total pressure on the rate constant, k, is shown in Fig. 5, the results of analyses are summarized in Table 2. The rate constant, k, increases along with the increases in the total pressure at the reaction temperatures of 104 and 124°C; on the other hand, at 84°C it reaches a maximum when the total pressure is 120 kg/cm², and then it tends to decrease slightly. The higher the total pressure and the lower the reaction temperature, the larger the α-MCP/β-MCP mole ratios are.

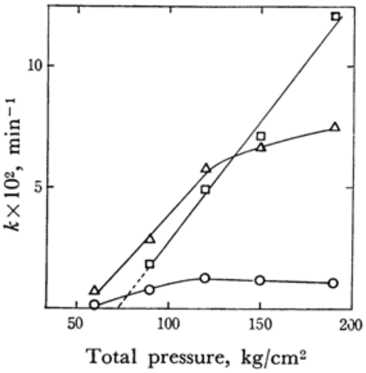

Fig. 5. The effect of total pressure on the rate constant k.

Reaction temperature °C	84	104	124
Mark	○	△	□

Thus the effect of the total pressure on the reaction rate and on the composition of products is found to be significant, but it will not be known whether this effect is due to a change in the partial pressure of carbon monoxide or of hydrogen until the effect of each of these partial pressures is examined; this will be done in the following paragraphs.

The Effect of the Respective Partial Pressures of Carbon Monoxide and Hydrogen. The experiments to examine the dependence of the reaction rate on the carbon monoxide partial pressure were carried out as follows. The reactions were carried out at several total pressures, *i. e.*, at 190, 150, 120, 90 and 60 kg/cm², the initial hydrogen partial pressure in each run being adjusted to about 10 kg/cm². The total pressure during the reaction was kept constant by supplying carbon monoxide containing 5% hydrogen, the hydrogen partial pressure during the reaction in each run being 10±2 kg/cm².

The effect of the hydrogen partial pressure on the reaction rate was tested as follows. The reactions were carried out at a fixed total pressure of 190 kg/cm², while the initial hydrogen partial pressures were varied between 3 and 25 kg/cm². Carbon monoxide with an appropriate content of hydrogen was supplied during the reaction, so that no deviation in the hydrogen partial pressure during the reaction was more than ±20% of the initial value. Although the initial partial pressure of carbon monoxide also varied in these experiments from 165 to 187 kg/cm², the effect of its variation within this range on the reaction rate was negligible, as is evident from Fig. 6.

The reactions were carried out at two different temperatures, 94 and 114°C; the rate constant, k, was calculated from the inclination of the initial plot of $\log C_0/C_t$ *vs.* the reaction time, as has been mentioned above, and was then plotted against the respective partial pressures of carbon monoxide and hydrogen, as is shown in Figs. 6 and 7. The rate constant, k, at 114°C does not change greatly with the carbon monoxide partial

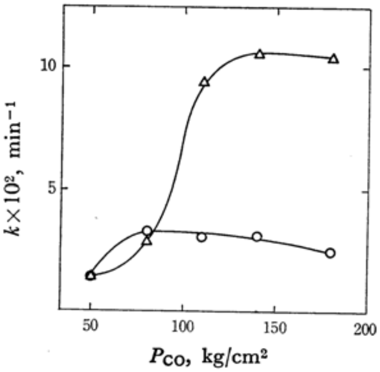

Fig. 6. The effect of carbon monoxide partial pressure on the rate constant k.

Reaction temperature °C	94	114
Mark	○	△

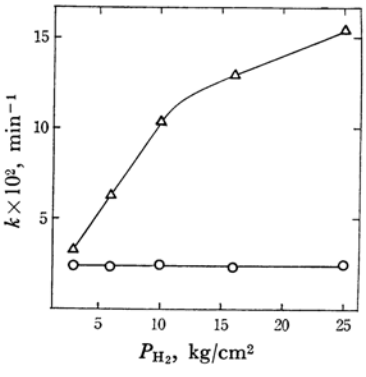

Fig. 7. The effect of hydrogen partial pressure on the rate constant k.

Reaction temperature °C	94	114
Mark	○	△

TABLE 3. THE EFFECT OF THE RESPECTIVE PARTIAL PRESSURES OF CARBON MONOXIDE AND HYDROGEN ON THE YIELDS OF PRODUCTS

4 mmol $Co_2(CO)_8$, 12 mmol Py, 0.5 mol AN, 2 mol methanol; reaction period, 1.0 hr

Expt. No.	Reaction temp. °C	Pressure a)	Amounts of products, mol					α/β
			AN	α-MCP	β-MCP	β-CPA	PN	
		P_{CO}, kg/cm^2						
38	94	50	0.198	0.201	0.071	0.002	0.004	2.8
39	94	80	0.030	0.367	0.093	0.005	0.003	3.9
40	94	110	0.038	0.388	0.063	0.003	0.004	6.2
41	94	140	0.047	0.396	0.051	0.002	0.003	7.8
42	114	50	0.188	0.161	0.079	0.016	0.010	2.0
43	114	80	0.006	0.309	0.139	0.015	0.009	2.2
44	114	110	0.004	0.323	0.135	0.022	0.007	2.4
45	114	140	0.003	0.340	0.128	0.020	0.006	2.7
		P_{H_2}, kg/cm^2						
46	94	3	0.207	0.255	0.019	0	0.003	13.4
47	94	6	0.076	0.381	0.033	0	0.004	11.6
48	94	16	0.060	0.357	0.030	0.002	0.004	11.9
49	94	25	0.006	0.384	0.036	0.003	0.005	10.7
50	114	3	0.007	0.407	0.081	0.002	0.003	5.0
51	114	6	0.003	0.376	0.102	0.001	0.003	3.7
52	114	16	0.002	0.357	0.085	0.021	0.006	4.2
53	114	25	0.001	0.338	0.087	0.029	0.006	3.9

a) In the experiments from No. 38 to 45 the hydrogen partial pressures were within the range 10± 2 kg/cm^2. The experiments from No. 46 to 53 were carried out at a fixed total pressure of 190 kg/cm^2.

pressure in the range from 110 to 180 kg/cm^2, but it decreases rapidly as the partial pressure decreases below 110 kg/cm^2. The rate constant, k, at 94°C decreases slowly as the carbon monoxide partial pressure increases above 80 kg/cm^2, but it decreases rapidly as the latter decreases below 80 kg/cm^2. The rate constant, k, at 114°C increases with the hydrogen partial pressure, while the rate constant, k, at 94°C is entirely independent of the hydrogen partial pressure.

The results of the analyses are summarized in Table 3. The α-MCP/β-MCP mole ratio increases as the carbon monoxide partial pressure increases, but it does not change significantly as the hydrogen partial pressure increases.

The Effect of the Catalyst Concentration. The reactions were carried out with 0.5 mol of AN, 2 mol of methanol and with several amounts of $Co_2(CO)_8$ (from 2 to 6 mmol) under a total pressure of 190 kg/cm^2, with the Py/$Co_2(CO)_8$ mole ratio kept constantly at 3. The effect of the catalyst concentration on the rate constant, k, is shown in Fig. 8, in which k is plotted against the amount of $Co_2(CO)_8$ (mole). Figure 8 reveals that the reaction is approximately first-order at 94°C, but that it is second-order at 114°C, with respect to $Co_2(CO)_8$.8)

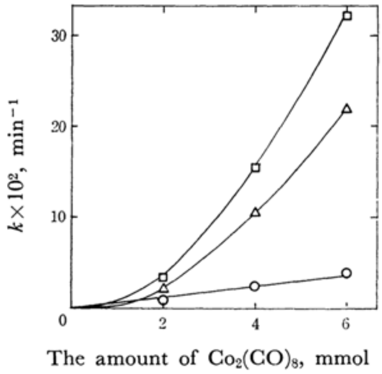

Fig. 8. The rate constant k plotted against the amount of $Co_2(CO)_8$, the mole ratio Py/$Co_2(CO)_8$ being constant.

Reaction temperature °C	94	114	114
Hydrogen partial pressure kg/cm^2	10	10	25
Mark	○	△	□

The Order of the Reaction with Respect to Methanol. In order to determine the order of the reaction with respect to methanol, the reactions were carried out with an excess of AN relative to methanol, *i. e.*, with 2 mol of AN to 0.5 mol of methanol. The amount of reacted methanol (mole) in this case can be equated with that of the supplied gas (mole), since no products other than α- and β-MCP are found upon the

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8) On plotting log k against the log of the amount of $Co_2(CO)_8$, the order of the reaction was found to be 1.3 at 94°C and 2.0 at 114°C.

analysis of the products after a 1 hr reaction.[9]

$$C_0' - C_t' = V_t \quad (5)$$

Here C_0' and C_t' are the amounts of methanol at inception and at the reaction time, *t*, respectively. Thus $C_0'-C_t'$ is calculated by Eq. (5) and is plotted against the reaction time in Fig. 9, which indicates that the reactions at both temperatures, *i. e.*, at 94 and 114°C, are zero order with respect to methanol.[10]

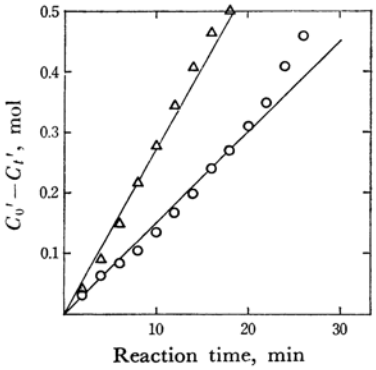

Fig. 9. The plot of the amount of reacted methanol, $C_0'-C_t'$, *vs.* reaction time, in the presence of excess AN. 0.5 mol Methanol, 2 mol AN, 4 mmol $Co_2(CO)_8$, 12 mmol Py, carbon monoxide containing 5% hydrogen were used. Total pressure 190 kg/cm².

Reaction temperature °C	94	114
Mark	○	△

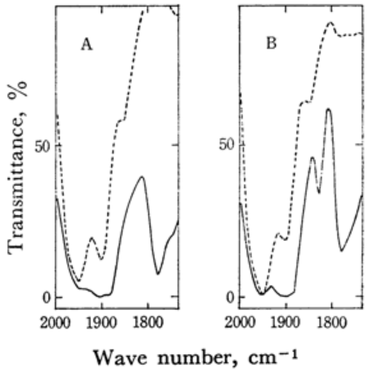

Fig. 10. Solutions made from 0.25 mol AN, 1 mmol $Co_2(CO)_8$ and 2 or 0 mmol Py were stirred in the autoclave at 94°C or at 114°C under the constant pressure (190 kg/cm²) of carbon monoxide containing 5% hydrogen for 15 min, and the samples were withdrawn from the autoclave for IR measurement.

A: at 94°C
B: at 114°C
Full lines: In the presence of Py
Dotted lines: In the absence of Py

The Structure of the Catalyst. The infrared spectra measured on various samples are shown in Fig. 10. The spectra of AN solutions of $Co_2(CO)_8$ treated without Py indicate no absorption due to the acyl group, whereas the absorption spectra of the same solutions treated with Py show acyl carbonyl bands, *i. e.*, a single band at 1778 cm⁻¹ for samples treated at 94°C and two bands, at 1778 and 1828 cm⁻¹, for samples treated at 114°C. This indicates that Py is necessary for the formation of acylcobalt carbonyls. The bands at 1778 and 1828 cm⁻¹ turned out to be due to β- and α-cyanopropionyl cobalt carbonyl respectively, since, when the samples treated at 94°C were heated with methanol, the mentioned single band at 1778 cm⁻¹ disappeared and only methyl β-cyanopropionate was detected in the resulting solution, while when the samples treated at 114°C were heated with methanol both the bands, at 1778 and at 1828 cm⁻¹, disappeared and methyl esters of β- and α-cyanopropionic acids were detected in the resulting solution. In the spectra of samples of the reacting solution containing methanol in addition to AN, $Co_2(CO)_8$, and Py, the bands due to acylcobalt carbonyls were absent; instead, strong absorptions due to esters appeared. This indicates that the acylcobalt carbonyls are instantaneously decomposed by methanol into esters in the reacting solution; this is in good agreement with the kinetic observation that the reaction is zero-order with respect to methanol. It is also revealed in Fig. 10 that the concentration of cobalt carbonyl anions (the band at 1900 cm⁻¹) is greatly

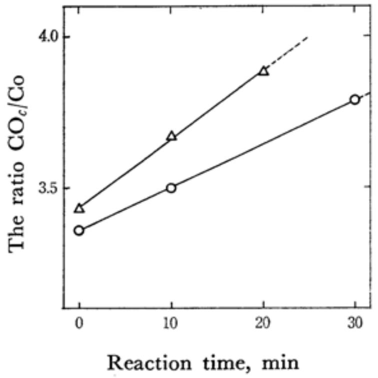

Fig. 11. The ratio CO_c/Co as function of reaction time. The reactions were carried out with 0.125 mol AN, 0.5 mol methanol, 1 mmol $Co_2(CO)_8$ and 3 mmol Py under the constant pressure (190 kg/cm²) of carbon monoxide containing 5% hydrogen.

Reaction temperature °C	94	114
Mark	○	△

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[9] The yields of α-MCP and β-MCP from methanol were 73 and 26% in the experiment carried out at 114°C, but 88 and 10% in the experiment at 94°C.

[10] It is not still known why the plots at the later stages of the reaction carried out at 94°C exceed even the line expected for a zero-order reaction.

increased by the addition of Py; this may be ascribed to the pyridinium salt of cobalt hydrocarbonyl.[11]

In order to determine the CO_c/Co ratio in the reacting state, the samples were withdrawn from the autoclave at definite intervals of time from the beginning of the reaction and analyzed. The results are plotted against the reaction time in Fig. 11. The ratio increases from the initial value of 3.3 or 3.4 to 4 with the progress of the reaction.

Discussion

From the above results it is obvious that the hydroesterification of AN in the presence of Py involves the formation of acylcobalt carbonyls, which then react with methanol to give methyl cyanopropionates and cobalt hydrocarbonyl. Since Py was found in the present study to be necessary for the formation of acylcobalt carbonyls, the structure of the intermediate acylcobalt carbonyl is presumably the Py complex of acylcobalt tricarbonyl; this is by analogy with the known triphenylphosphine complex of acylcoblat tricarbonyl.[12] From the findings that the Arrhenius plots of the rate constants, k, bend downward at about 100°C, provided the reactions are carried out with a fixed $Py/Co_2(CO)_8$ mole ratio of 2, 3 or 4, and that the isomer ratios of the products differ markedly between the reactions carried out at temperatures above and below 100°C, it is clear that there must be a difference between the mechanism of the reaction at temperatures above 100°C and that at temperatures below 100°C. Therefore, the mechanisms of the reactions carried out above and below 100°C will be discussed separately.

The Mechanism of the Reaction at Temperatures above 100°C. The first step in the reaction is considered to be the direct addition of $HCo(CO)_4$ to AN, since the rate constant, k, increases with the hydrogen partial pressure and is first-order with respect to AN.

The reaction scheme may be postulated as follows.

$$\mathrm{AN} + \mathrm{HCo(CO)_4} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{NC\text{-}C_2H_4Co(CO)_4} \qquad (1')$$

$$\mathrm{NC\text{-}C_2H_4Co(CO)_4} + \mathrm{Py} \xrightarrow{k_3} \mathrm{NC\text{-}C_2H_4COCo(CO)_3(Py)} \qquad (2')$$

$$\mathrm{NC\text{-}C_2H_4COCo(CO)_3(Py)} + \mathrm{CH_3OH} \rightarrow \mathrm{NC\text{-}C_2H_4COOCH_3} + \mathrm{HCo(CO)_3} + \mathrm{Py} \qquad (3')$$

$$\mathrm{HCo(CO)_3} + \mathrm{CO} \xrightarrow{k_4} \mathrm{HCo(CO)_4} \qquad (4')$$

Here, the step (3′) is not rate-determining, since the reaction is zero-order in methanol. Therefore, the overall rate, v, may be expressed as in Eq. (6):

$$v = k_1[\mathrm{AN}][\mathrm{HCo(CO)_4}] - k_2[\mathrm{NC\text{-}C_2H_4Co(CO)_4}] \qquad (6)$$

By the steady-state approximation for the concentration of the intermediate, Eq. (7) is obtained:

$$k_1[\mathrm{AN}][\mathrm{HCo(CO)_4}] = [\mathrm{NC\text{-}C_2H_4Co(CO)_4}](k_2+k_3[\mathrm{Py}]) \qquad (7)$$

By subtracting $[\mathrm{NC\text{-}C_2H_4Co(CO)_4}]$ from Eqs. (6) and (7), the overall rate, v, is expressed as follows:

$$v = k_1k_3[\mathrm{AN}][\mathrm{HCo(CO)_4}][\mathrm{Py}]/(k_2+k_3[\mathrm{Py}]) \qquad (8)$$

According to Eq. (8), v is first-order in AN, in $HCo(CO)_4$, and in Py, provided that k_2 is much larger than $k_3[Py]$. The fact that the reaction rate increases with an increase in the hydrogen partial pressure is consistent with Eq. (8), since the concentration of $HCo(CO)_4$ necessarily increases with an increase in the hydrogen partial pressure. If it is assumed that the concentration of $HCo(CO)_4$ is directly proportional to the amount of $Co_2(CO)_8$ added before the reaction, v must be second-order with respect to the catalyst concentration when the $Py/Co_2(CO)_8$ ratio is constant, since v is first-order in $HCo(CO)_4$ and in Py according to Eq. (8), as has been established above. This is in agreement with the experimental results.

If the steady state for the concentration of $HCo(CO)_3$ is assumed, the rate of the step (4′) is equal to the overall rate, v:

$$v = k_4[\mathrm{HCo(CO)_3}]P_{\mathrm{CO}} \qquad (9)$$

According to Eq. (9), the concentration of $HCo(CO)_3$ must be proportional to the overall rate, v, which is largest at inception and which gradually decreases until it approaches zero at the end of the reaction. Hence, the mean number of carbon monoxide attached to cobalt (CO_c/Co) should be smallest at inception and should increase until it approaches 4 at the end of the reaction; this is in agreement with the results of Fig. 11. Thus, all the kinetic results and the results of Fig. 11 can be understood on the basis of Eqs. (8) and (9).

On considering the analytical results it can be said that both α- and β-MCP are produced by this mechanism at reaction temperatures above 100°C; this is consistent with the findings of the IR study that both α- and β-cyano-isomers of acylcoblat carbonyl were found in the AN solution of $Co_2(CO)_8$ and Py treated under the same conditions (114°C, 190 kg/cm^2), but in the absence of methanol.

The Mechanism of the Reaction at Temperatures below 100°C. The first step of the

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[11] The absorption at 1950 cm^{-1} is due to acrylonitrile.

[12] R. F. Heck, *J. Am. Chem. Soc.*, **84**, 2499 (1962).

reaction in this case must not be the direct addition of $HCo(CO)_4$ to AN; instead, it is considered to be the reaction between AN and $Co(CO)_4$ (or $Co_2(CO)_8$) to form an AN complex (probably a π complex) of cobalt tricarbonyl, since the rate constant, k, is quite independent of the hydrogen partial pressure, with which the concentration of $HCo(CO)_4$ necessarily increases and since, moreover, there is a slight downward trend in the rate constant as the carbon monoxide partial pressure is increased.

The reaction scheme may be postulated as follows:

$$Co(CO)_4 + AN \underset{k_2'}{\overset{k_1'}{\rightleftharpoons}} Co(CO)_3(AN) + CO \qquad (1'')$$

$$Co(CO)_3(AN) + HCo(CO)_4 \underset{k_4'}{\overset{k_3'}{\rightleftharpoons}} NC\text{-}C_2H_4Co(CO)_4 + Co(CO)_3 \qquad (2'')$$

$$NC\text{-}C_2H_4Co(CO)_4 + Py \overset{k_5'}{\rightarrow} NC\text{-}C_2H_4COCo(CO)_3(Py) \qquad (3'')$$

$$NC\text{-}C_2H_4COCo(CO)_3(Py) + CH_3OH \rightarrow NC\text{-}C_2H_4COOCH_3 + HCo(CO)_3 + Py \qquad (4'')$$

$$Co(CO)_3 + CO \overset{k_6'}{\rightarrow} Co(CO)_4 \qquad (5'')$$

$$HCo(CO)_3 + CO \overset{k_7'}{\rightarrow} HCo(CO)_4 \qquad (6'')$$

Here, the step (4'') is not rate-determining, since the reaction is zero-order in methanol. Therefore, the overall rate, v may be expressed as Eq. (10):

$$v = k_5'[NC\text{-}C_2H_4Co(CO)_4][Py] \qquad (10)$$

By the steady-state approximation for the concentrations of the intermediates, Eqs. (11) and (12) are obtained:

$$\begin{aligned} &k_1'[Co(CO)_4][AN] \\ &\quad + k_4'[NC\text{-}C_2H_4Co(CO)_4][Co(CO)_3] = \\ &\quad [Co(CO)_3(AN)](k_2'P_{CO} + k_3'[HCo(CO)_4]) \end{aligned} \qquad (11)$$

$$\begin{aligned} &k_3'[Co(CO)_3(AN)][HCo(CO)_4] \\ &\quad = [NC\text{-}C_2H_4Co(CO)_4](k_4'[Co(CO)_3] \\ &\quad + k_5'[Py]) \end{aligned} \qquad (12)$$

By subtracting $[Co(CO)_3(AN)]$ and $[NC\text{-}C_2H_4Co(CO)_4]$ from Eqs. (10), (11) and (12), the overall rate, v, is expressed as follows:

$$v = \frac{k_1'k_3'k_5'[AN][Co(CO)_4][HCo(CO)_4][Py]}{\begin{pmatrix} k_2'k_4'P_{CO}[Co(CO)_3] + k_5'[Py] \\ \times (k_2'P_{CO} + k_3'[HCo(CO)_4]) \end{pmatrix}} \qquad (13)$$

Here, if the second term in the denominator is assumed to be much larger than the first one, Eq. (14) is obtained:

$$v = \frac{k_1'k_3'[AN][Co(CO)_4][HCo(CO)_4]}{k_2'P_{CO} + k_3'[HCo(CO)_4]} \qquad (14)$$

Equation 14 accounts for the facts that the rate is independent of the hydrogen partial pressure, that it decreases slightly as the carbon monoxide partial pressure is increased, and that the reaction is zero-order in Py when $Py/Co_2(CO)_8$ is in the range from 1 to 4.[13]

When, on the other hand, [Py] is very small, the second term in the denominator of Eq. (13) can be neglected and Eq. (15) is obtained; this accounts for the fact that the rate is increased by the addition of an amount of Py as amall as 1 in terms of the $Py/Co_2(CO)_8$ mole ratio.

$$v = \frac{k_1'k_3'k_5'[AN][Co(CO)_4][HCo(CO)_4][Py]}{k_2'k_4'P_{CO}[Co(CO)_3]} \qquad (15)$$

If the steady states for the concentrations of $Co(CO)_3$ and $HCo(CO)_3$ are assumed, the rates of the steps (5'') and (6'') are equal to v:

$$v = k_6'[Co(CO)_3]P_{CO} = k_7'[HCo(CO)_3]P_{CO} \qquad (16)$$

According to Eq. (16), the concentrations of $Co(CO)_3$ and $HCo(CO)_3$ must be largest at inception and decrease until they approach zero at the end of the reaction, as has been already mentioned in the case of reactions above 100°C. This is in agreement with the results of Fig. 11. Thus, all the kinetic results and the results of Fig. 11 can be understood on the basis of Eqs. (13) and (16).

It can be said, after considering the results of analyses, that α-MCP is selectively produced by this mechanism at reaction temperatures below 100°C. However, the acylcobalt carbonyl, which was found in the AN solution of $Co_2(CO)_8$ and Py treated under the same conditions (94°C, 190 kg/cm^2) but in the absence of methanol, was exclusively that of the β-cyano isomer. For this contradiction there are two possible explanations to be considered. One is that the acylcobalt carbonyl found is not the real intermediate of the reaction; another kind of acylcobalt carbonyl (the real intermediate) is generated on the addition of methanol. The other possible explanation is that the isomerization of the β - into the α-cyano isomer takes place rapidly in the intermediate acylcobalt carbonyl upon the addition of methanol, as has been stated by Takegami *et al.*, *i. e.*, that the isomerization of butyryl-cobalt carbonyls occurs in polar solvents.[14] There is not yet experimental evidence to decide which of the above two explanations is most reasonable.

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[13] The fact that the rate constant, k, tends to decrease as the $Py/Co_2(CO)_8$ ratio is increased above 2 may be ascribed to the formation of the pyridinium salt of cobalt hydrocarbonyl, which has been found by IR study to increase upon the addition of Py.

[14] Y. Takegami, C. Yokokawa and Y. Watanabe, This Bulletin, **38**, 787 (1965).

Although it is revealed in Table 3 that the carbon monoxide partial pressure has a remarkable effect on the α-MCP/β-MCP ratio in both temperature ranges, the reason for this can not fully be understood at the present stage of this investigation.

Summary

The cobalt carbonyl-catalyzed hydroesterification of acrylonitrile with carbon monoxide and methanol can be successfully carried out in the presence of a small amount of hydrogen and a limited amount of pyridine. Methyl esters of α- and β-cyanopropionic acids are produced, the former in a larger amount than the latter. The reaction mechanisms at temperatures below and above 100°C are different; the selectivity to methyl α-cyanopropionate is much larger at reaction temperatures below 100°C than above 100°C. The mechanisms of the reactions at temperatures above and below 100°C have been discussed separately.

The author is indebted to Dr. Kenichiro Bando for his discussions.