BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1876—1883 (1968)

The Cobalt Carbonyl-catalyzed Intramolecular Hydroesterification of Allyl Alcohol with Carbon Monoxide

Akio MATSUDA

Government Chemical Industrial Research Institute, Tokyo, Mita, Meguro-ku, Tokyo

(Received November 1, 1967)

The intramolecular hydroesterification of allyl alcohol with carbon monoxide to give γ-butyrolactone occurred in the presence of cobalt carbonyl under the pressure of carbon monoxide containing a small amount of hydrogen; propionaldehyde and isobutyraldehyde were produced as by-products. The selectivity toward γ-butyrolactone increased with the use of acetonitrile or its derivatives as the solvent. The addition of pyridine, in the absence of these solvents, was effective only in increasing the reaction rate, not in increasing the selectivity toward γ-butyrolactone. On the other hand, in the presence of acetonitrile as a solvent, the selectivity toward γ-butyrolactone increased together with the reaction rate when a catalytic amount of an organic base such as pyridine was added. The higher the reaction temperature, the higher the pressure necessary to attain a maximum selectivity toward γ-butyrolactone; the best yield of γ-butyrolactone was *ca.* 60%. The effect of the partial pressures of hydrogen and carbon monoxide on the initial rate of the formation of each product was made clear. The experimental results were explained by a mechanism involving two different paths for the formation of an alkylcobalt carbonyl-intermediate. The order of effectiveness of acetonitrile and its derivatives as solvents has been interpreted in terms of the HSAB principle by Pearson *et al.*

In a preceding paper on the cobalt carbonyl-catalyzed hydroesterification of acrylonitrile with carbon monoxide and methanol, it was reported that the reaction carried out in the presence of a small amount of hydrogen proceeded rapidly upon the addition of as little pyridine (Py) as 1—4 in terms of the Py/$Co_2(CO)_8$ mole ratio, and that the reaction resulted in a high yield of methyl cyanopropionate, while in the absence of Py the reaction proceeded very little.[1]

In the present study, the possibility of using this method for the synthesis of hydroxymethylbutyrate from allyl alcohol, carbon monoxide, and methanol was first tested. As a result, the intramolecular hydroesterification of allyl alcohol with carbon monoxide to give γ-butyrolactone, the isomerization of allyl alcohol to give propionaldehyde, and the hydroformylation of allyl alcohol with carbon monoxide and hydrogen to give β-hydroxyisobutyraldehyde, which can then be readily dehydrated and hydrogenated into isobutyraldehyde, were found to occur, but not the expected hydroesterification of allyl alcohol with carbon monoxide and methanol to give hydroxy-methylbutyraet.

Adkins and Kresk tested the hydroformylation of allyl alcohol with carbon monoxide and hydrogen and obtained γ-hydroxy-butyraldehyde.[2]

Goetz and Orchin studied the isomerization of allyl alcohol with cobalt hydrocarbonyl, which gave propionaldehyde.[3]

The report by Falbe concerning the ring-closure reactions with carbon monoxide describes the reaction between allyl alcohol and carbon monoxide in the presence of dicobalt octacarbonyl, but the yield of the resulting γ-butyrolactone is reported to be as little as 2%.[4]

The aim of the present investigation, in this connection, is directed at obtaining γ-butyrolactone in as good an yield as possible by the intramolecular hydroesterification of allyl alcohol with carbon monoxide. The synthesis of γ-butyrolactone from allyl alcohol and carbon monoxide may be interesting from

---

[1] A. Matsuda, This Bulletin, **40**, 135 (1967).

[2] H. Adkins and G. Kresk, *J. Am. Chem. Soc.*, **70**, 383 (1948).

[3] R. W. Goetz and M. Orchin, *ibid.*, **85**, 1549 (1963).

[4] J. Falbe, *Angew. Chem.*, **78**, 532 (1966).

an industrial point of view. Moreover, the present reaction may be convenient for determining the factors governing the rate of double-bond isomerization and the factors governing the rate of carbonylation, because, as was pointed out by Goetz *et al.*,[3] if the double-bond isomerization of allyl alcohol should occur, the isomerized product would tautomerize rapidly to propionaldehyde, so equilibrium reactions are unlikely.

Experimental

Such reagents as allyl alcohol, acetonitrile, and pyridine were obtained commercially and rectified before use, except for nicotine and nicotinic acid, which were used without rectification. The synthesis gas was prepared by mixing carbon monoxide with an appropriate amount of hydrogen so that the desired percentage of hydrogen could be obtained. Carbon monoxide and dicobalt octacarbonyl were prepared by the procedure described previously.[5]

The reactions were carried out in a 100-cc stainless-steel autoclave equipped with a magnetic up-and-down stirrer, using essentially the same procedure as was described previously.[1] The reaction temperature was controlled within a range of ±1°C. In the case of the constant-pressure experiment, the synthesis gas was automatically supplied by means of a pressure regulator from a pressure storage vessel in order to keep the total pressure constant throughout the reaction. The amount of gas supplied during the reaction was calculated from the pressure drop in the pressure storage. Experiments at pressures over 300 kg/cm^2 were carried out with another apparatus, one which had been designed for use at pressures of 1000 kg/cm^2, but the method of the experiments was essentially the same as in the case of experiments at pressures lower than 300 kg/cm^2, except that the pressure level in the pressure storage was recorded during the reaction by means of a Strain gauge for the sake of accuracy.

The product composition was quantitatively determined by the gas chromatographical method: the γ-butyrolactone was analyzed with a 3-m column of ethyleneglycol-adipic acid polyester by adding octylacetate, as an internal standard, to the reaction product at the temperature of 200°C, while lower-boiling components, such as propionaldehyde, isobutyraldehyde, and allylalcohol, were analyzed with a 3-m column of ethyleneglycol-adipic acid polyester plus a 2-m column of dioctylphthalate by adding toluene as an internal standard at the temperature of 100°C.

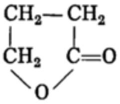
Results

The Effect of Solvents. Preliminary experiments carried out under conditions similar to those of Table 1 showed that the yield of γ-butyrolactone was larger in the absence of a solvent than in the presence of such a solvent as methanol and benzene; they thus suggested that a solvent might have some effect, whether positive or negative, on the selectivity of the reaction. Experiments were, therefore, carried out with various kinds of solvents in order to test their effects, the Py/$Co_2(CO)_8$ mole ratio being kept constant at the optimum value of 1. The results are summarized in Tables 1 and 2.

Solvents such as acetonitrile and its derivatives, as can be seen from Tables 1 and 2,

TABLE 1. THE EFFECT OF SOLVENT (I)

4 mmol $Co_2(CO)_8$, 4 mmol Py, 1/4 mol allyl alcohol; total pressure, 300 (initial)—*ca.* 200 kg/cm^2; reaction temperature, 100°C; hydrogen content of the gas used, 11%

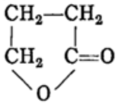
Solvent	mol	Reaction time min	Conversion mol%	Selectivity toward each product (mol%)			
					C_2H_5CHO	$i\text{-}C_3H_7CHO$	Residue
None	0	60	98	42	15	6.9	36
CH_3CN	0.04	60	97	45	13	7.9	34
CH_3CN	0.1	60	92	49	12	8.5	30
CH_3CN	0.2	60	88	56	11	8.0	25
CH_3CN	0.5	135	91	57	12	8.1	23
CH_3CH_2CN	0.07	60	95	52	15	9.7	23
$(CH_3)_2CHCN$	0.06	60	90	47	14	6.2	33
C_6H_5CN	0.1	60	94	38	12	8.4	42
$n\text{-}C_3H_7CHO$	0.1	60	93	41	21	4.8	33
C_6H_6	0.1	60	98	38	24	6.4	32
CH_3OH	0.2	60	91	38	27	7.8	27

---

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

TABLE 2. THE EFFECT OF SOLVENT (II)

4 mmol $Co_2(CO)_8$, 4 mmol Py, 1/4 mol allyl alcohol; total pressure, 100 kg/cm^2; reaction temperature, 100°C; hydrogen content of the gas used, 14%

Solvent	mol	Reaction time min	Initial rate$\times10^3$ mol/min[a]	Conversion mol%	Selectivity toward each product (mol%) 			
						C_2H_5CHO	i-C_3H_7CHO	Residue
None	0	60	8.8	98	38	28	3.3	31
CH_3CN	1/8	45	7.0	97	49	23	3.0	25
CH_3CN	1/2	60	5.5	93	58	17	4.3	21
CH_3CH_2CN	1/8	55	6.4	98	47	20	3.6	29
CH_3CH_2CN	1/2	60	6.1	95	55	19	3.0	23
$(CH_3)_2CHCN$	1/8	55	6.9	98	51	22	3.9	23
$(CH_3)_2CHCN$	1/2	60	4.9	96	53	26	3.2	18
$NC(CH_2)_4CN$	1/8	120	4.3	98	50	15	3.0	32
CH_3OCH_2CN	1/8	60	3.3	92	50	20	3.1	27
$HOCH_2CN$	1/8	100	3.5	83	55	14	1.7	29
$C_6H_5CH_2CN$	1/8	100	3.9	98	49	21	3.9	26
$HCOOCH_3$	1/8	60	4.1	93	42	31	3.2	24
$(C_2H_5)_2O$	1/8	60	6.1	99	34	47	4.6	14
Dioxane	1/8	60	3.4	95	37	45	5.3	13

a) The amount of gas supplied during the initial 10 min is listed in Tables 2—6 as a rough measure of the initial rate.

are effective in increasing the selectivity toward γ-butyrolactone and in decreasing the selectivity toward propionaldehyde and the residue, but the reaction rate is decreased by these solvents; these effects are apt to be enhanced by the use of a larger amount of such a solvent. Benzonitrile, unlike acetonitrile or its derivatives, has no effect on the selectivity toward γ-butyrolactone.

The effectiveness of such acetonitrile derivatives as $HOCH_2CN$, CH_3OCH_2CN, and $C_6H_5CH_2CN$ in increasing the selectivity toward γ-butyrolactone decreases in the order $HOCH_2CN > CH_3OCH_2CN > C_6H_5CH_2CN$. When methyl-substituted acetonitriles are used as solvents, the above effectiveness decreases as the number of methyl-substitution increases, *i.e.*, in the order $CH_3CN > CH_3CH_2CN > (CH_3)_2CHCN$.

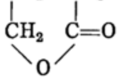
Aldehyde and formic esters as solvents have almost no effect on the selectivity toward γ-butyrolactone. Such ethers as diethyl ether and dioxane, however, when used as solvents increase the selectivity toward propionaldehyde and decrease the selectivity toward γ-butyrolactone. Methanol and benzene also increase the selectivity toward propionaldehyde and decrease the selectivity toward γ-butyrolactone, but their effects are smaller than those of ethers.

The Effect of Acetonitrile as a Solvent and the Effect of the Addition of Py and Other Organic Bases. The selectivity toward γ-butyrolactone has thus been found to increase remarkably with the use of acetonitrile as a solvent and with the use of an amount of Py equimolar to $Co_2(CO)_8$. Experiments were then carried out in the absence of both acetonitrile and Py, in the presence of acetonitrile and no Py, in the presence of Py and no acetonitrile, in the presence of acetonitrile with various amounts of Py, and in the presence of acetonitrile with various kinds of bases other than Py. The results are shown in Table 3.

Evidently, the addition of Py increases the reaction rate, it but does not by itself affect the selectivity, while acetonitrile, when used as a solvent, is, even in the absence of Py, effective in increasing the selectivity toward γ-butyrolactone and in decreasing the selectivity toward propionaldehyde and the residue. Clearly, acetonitrile is effective in increasing the selectivity toward γ-butyrolactone simply because it retards the formation of propionaldehyde and the residue, not because it accelerates the formation of γ-butyrolactone, for Tables 2 and 3 indicate that the reaction rate rather decreases upon the use of acetonitrile as a solvent. Both the reaction rate and the selectivity toward γ-butyrolactone, in the presence of acetonitrile as a solvent, increase as the amount of Py is increased, reach maxima when the $Py/Co_2(CO)_8$ mole ratio is

TABLE 3. THE EFFECT OF ACETONITRILE AS A SOLVENT AND THE ADDITION OF ORGANIC BASES

4 mmol $Co_2(CO)_8$, 1/4 mol allyl alcohol; total pressure 100 kg/cm²; reaction temperatue 100°C; reaction time 1.0 hr; hydrogen content of the gas used, 14%

					Selectivity toward each product (mol%)			
CH_3CN mol	Organic base	mmol	Initial rate×10³ mol/min[a)]	Conversion mol%		C_2H_5CHO	i-C_3H_7CHO	Residue
0	None	0	2.6	99	35	21	3.3	41
0	Py	4	8.8	98	38	28	3.3	31
0.5	None	0	3.2	78	49	17	2.2	32
0.5	Py	2	4.3	94	54	17	3.7	25
0.5	Py	4	5.5	93	58	17	4.3	21
0.5	Py	6	4.9	87	55	18	4.2	23
0.5	Quinoline	4	5.0	92	54	19	2.8	24
0.5	Nicotinic acid	4	4.8	93	54	18	6.5	21
0.5	Nicotine	2	5.0	93	56	18	2.9	23
0.5	Piperidine	2	4.8	93	55	17	2.2	26
0.5	Pyrrolidine	2	4.2	93	53	18	2.7	26
0.5	*N*, *N*-Dimethyl propionamide	2	3.2	86	51	16	1.6	31

a) *Cf.* Table 2.

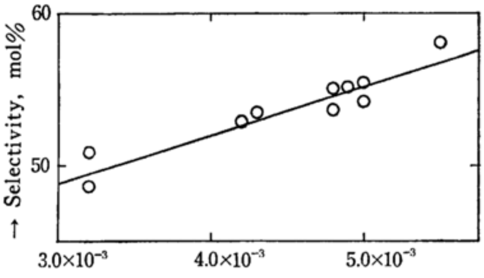


Fig. 1. The relation between the selectivity toward γ-butyrolactone and the initial rate.

1, and then decline. In fact, from the results of experiments carried out with acetonitrile as a solvent in the presence of various amounts of Py or other organic bases, an almost linear relation between the reaction rate and the selectivity toward γ-butyrolactone was obtained, as is shown in Fig. 1. This means that the intramolecular hydroesterification, in the presence of acetonitrile as a solvent, is fairly selectively accelerated by the addition of Py or other organic bases.

The Effect of Pressure and Temperature. The results of experiments which were carried out under various pressures at the constant temperatures of 100, 120, and 130°C are shown in Tables 4 and 5. Clearly the selectivity toward propionaldehyde decreases as the pressure increases, while that toward isobutyraldehye increases. The selectivity toward γ-butyrolactone reaches its maximum at a certain pressure, which increases along with the temperature; the pressure for the best selectivity is 100 kg/cm² at 100°C, 300 kg/cm² at 120°C, and 500 kg/cm² at 130°C.

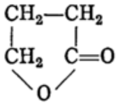
The results of the experiments carried out under the constant pressures of 400, 600, and 800 kg/cm² at various temperatures are shown in Table 6. Clearly the selectivity toward propionaldehyde increases along with the temperature. The higher the pressure, the higher the optimum temperature for attaining the best selectivity toward γ-butyrolactone; it is 130°C under 400 kg/cm², 140°C under 600 kg/cm², and in the 150—160°C range under 800 kg/cm².

The Effects of the Partial Pressures of Hydrogen and Carbon Monoxide. In order to understand the effect of the total pressure on the rate of the formation of each product, the effects of the partial pressures of hydrogen and carbon monoxide must be examined.

Constant-pressure experiments were carried out at 120°C with 1/4 mol of allyl alcohol, 1/2 mol of acetonitrile, 2 mmol of $Co_2(CO)_8$, and 2 mmol of Py, the composition of the synthesis gas used and the total pressure being varied so that the desired initial partial pressures of hydrogen and carbon monoxide could be attained. Aliquots of the reacting solution were withdrawn from the autoclave at definite intervals of time from the beginning of the reaction and were analyzed in order to

TABLE 4. THE EFFECT OF TOTAL PRESSURE (I)

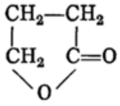
4 mmol $Co_2(CO)_8$, 4 mmol Py, 1/4 mol allyl alcohol, 1/2 mol acetonitrile; reaction time 1.0 hr; hydrogen content of the gas used, 14%

Total pressure kg/cm^2	Reaction temp. °C	Initial rate×10^3 mol/min[a]	Conversion mol %	Selectivity toward each product (mol%)			
					C_2H_5CHO	i-C_3H_7CHO	Residue
50	100	5.8	93	49	26	3.3	22
100	100	5.5	93	58	17	4.3	21
150	100	5.2	88	53	13	5.9	28
200	100	4.9	83	52	11	7.2	30
250	100	3.8	80	52	8.9	8.0	31
300	100	—	77	51	8.5	9.9	31
100	120	12.6	99	51	28	4.7	16
250	120	14.7	100	56	16	7.6	20
300	120	13.7	99	60	12	10	18
400	120	—	99	50	14	12	24

a) *Cf.* Table 2.

TABLE 5. THE EFFECT OF TOTAL PRESSURE (II)

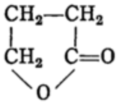
2 mmol $Co_2(CO)_8$, 2 mmol Py, 1/4 mol allyl alcohol, 1/2 mol acetonitrile; reaction time 1.0 hr; hydrogen content of the gas used, 10%

Total pressure kg/cm^2	Reaction temp. °C	Initial rate×10^3 mol/min[a]	Conversion mol %	Selectivity toward each product (mol%)			
					C_2H_5CHO	i-C_3H_7CHO	Residue
300	130	6.1	98	51	17	4.1	28
400	130	6.8	98	52	16	6.0	26
500	130	6.6	97	54	15	7.9	23
600	130	5.9	95	52	13	8.6	26

a) *Cf.* Table 2.

TABLE 6. THE EFFECT OF RECATION TEMPERATURE

1/4 mol allyl alcohol, 1/2 mol acetonitrile; Py/$Co_2(CO)_8$ 8 mole ratio, 1; hydrogen content of the gas used, 4%

Reaction temp. °C	Total press. kg/cm^2	Py mmol	Reaction time min	Initial rate×10^3 mol/min[a]	Conversion mol %	Selectivity toward each product (mol%)			
							C_2H_5CHO	i-C_3H_7CHO	Residue
120	400	4	60	6.5	95	53	11	3.3	33
130	400	4	60	12.1	98	61	19	4.5	16
140	400	2	60	—	99	57	30	4.1	9
130	600	4	60	7.2	97	51	16	6.0	27
140	600	2	60	6.2	99	56	19	4.8	20
150	600	2	30	13.6	98	53	24	3.7	19
150	800	1	60	5.8	94	54	19	5.3	22
160	800	1	60	8.2	99	54	25	5.1	16
170	800	1	30	12.9	98	46	39	4.8	10

a) *Cf.* Table 2.

determine the individual products. Examples of the plot of the yields of individual products against the reaction time are shown in Fig. 2. In Table 7 are summarized the initial rates calculated on the basis of results of analyses of samples withdrawn at the reaction time of 20 min; the initial rates of the formation of γ-butyrolactone, propionaldehyde, and isobutyraldehyde are denoted by v_1, v_2, and v_3 respectively. The specific increments of the initial rates of the formation of individual products caused by a unit increase in the hydrogen partial pressure, $\varDelta v_{1,2,3}/v_{2,2,3}\varDelta P_{H_2}$, and those caused by a unit increase in the carbon monoxide partial pressure, $\varDelta v_{1,2,3}/v_{1,2,3}\varDelta P_{CO}$, were calculated from Table 7; Table 8 lists the specific increment of v caused by a 10 kg/cm² increase in P_{H_2}($10\varDelta v_{1,2,3}/v_{1,2,3}\cdot\varDelta P_{H_2}$), and the specific increment of v caused by a 100 kg/cm² increase in P_{CO} ($100\varDelta v_{1,2,3}/v_{1,2,3}\varDelta P_{CO}$). It is clear from Table 8 that v_1, v_2, and v_3 all increase along with increases in the hydrogen partial pressure, v_3 increasing most conspicuously; that v_1 and v_2 decrease with increases in the carbon monoxide partial pressure, v_2 decreasing more than v_1, and that v_3 is essentially independent of the carbon monoxide partial pressure.

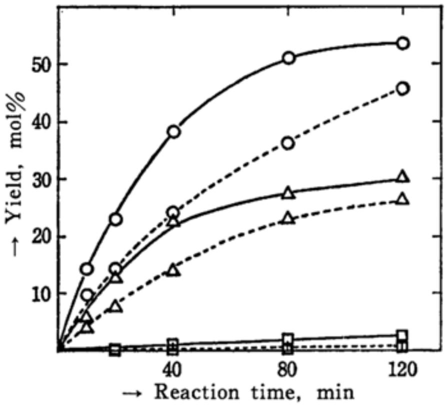


Fig. 2. The plot of the yields of individual products *vs.* the reaction time.
Full line: Expt. No. 2
Dotted line: Expt. No. 1
-○- : γ-Butyrolactone
-△- : Propionaldehyde
-□- : Isobutyraldehyde

Discussion

Since the rates of the formation of γ-butyrolactone, propionaldehyde, and isobutyraldehyde all increase with increases in the hydrogen partial pressure, cobalt hydrocarbonyl evidently plays a part in each of these formations. The cobalt hydrocarbonyl-catalyzed isomerization of allyl alcohol is assumed to take place through the hydrogen-shift in an intermediate π-complex, which is formed between coordinately-unsaturated cobalt hydrotricarbonyl and allyl alcohol, just as is usually assumed in the case of the metal carbonyl-catalyzed isomerization of olefins.[6,7]

Since the overall reaction rate in the present experiment decreases with an increase in the carbon monoxide partial pressure, the first step of the reaction would involve, at least partially, the formation of cobalt hydrotricarbonyl, as was proposed by Heck *et al.* to

TABLE 7. THE EFFECT OF THE RESPECTIVE PARTIAL PRESSURES OF HYDROGEN AND CARBON MONOXIDE ON THE INITIAL RATE OF FORMATION OF EACH PRODUCT

Expt. No.		1	2	3	4	5	6	7
H_2 content of the gas, %		6	10	6	10	6	10	6
Total pressure, kg/cm²		100	104	250	261	160	180	300
P_{H_2} (initial), kg/cm²		6	10	15	26	10	18	18
P_{CO} (initial), kg/cm²		94	94	235	235	150	162	282
Initial rate of formation, mmol/min	V_1	1.8	2.9	2.1	2.8	2.1	2.9	1.7
	$10\,V_2$	9.4	16	5.6	7.4	8.7	7.4	3.5
	$100\,V_3$	1.9	3.9	6.3	19	4.9	9.6	8.9

TABLE 8. SPECIFIC INCREMENTS CALCULATED FROM TABLE 7

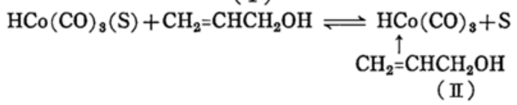
P_{CO}, kg/cm²	$10\varDelta V_1/V_1\varDelta P_{H_2}$	$10\varDelta V_2/V_2\varDelta P_{H_2}$	$10\varDelta V_3/V_3\varDelta P_{H_2}$
94	1.5	1.8	2.6
235	0.30	0.29	1.8
P_{H_2}, kg/cm²	$100\varDelta V_1/V_1\varDelta P_{CO}$	$100\varDelta V_2/V_2\varDelta P_{CO}$	$100\varDelta V_3/V_3\varDelta P_{CO}$
10	−0.49	−0.81	+0.46
18	−0.34	−0.44	−0.061

---

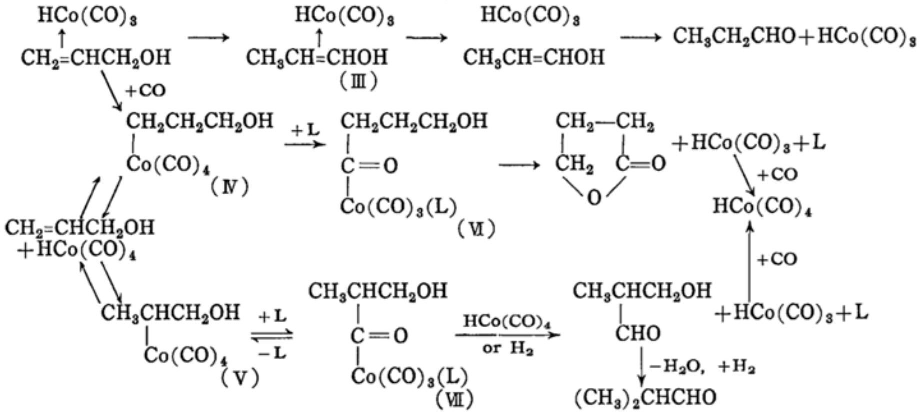
[6] T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

[7] F. Asinger, B. Fell and K. Schrage, *Chem. Ber.*, **98**, 372 (1965).

$$HCo(CO)_4 + S \rightleftharpoons \underset{(\mathrm{I})}{HCo(CO)_3(S)} + CO \qquad (1)$$



$$HCo(CO)_3(S) + CH_2{=}CHCH_2OH \rightleftharpoons \underset{(\mathrm{II})}{\overset{HCo(CO)_3}{\underset{CH_2=CHCH_2OH}{\uparrow}}} + S \qquad (2)$$



explain the inhibition by CO of the reaction of cobalt hydrotetracarbonyl with olefins.[8]

In a preceding paper on the hydroesterification of acrylonitrile,[1] two separate paths were proposed for the formation of alkylcobalt tetracarbonyl; one was the direct addition of $HCo(CO)_4$ to acrylonitrile, while the other was the path which goes through an acrylonitrile π-complex. In the present paper, also, the reaction mechanism will be discussed taking into account the possibility of the two separate above-mentioned paths.

The catalytic mechanism shown below can explain the experimental results; S denotes a solvent such as acetonitrile, while L denotes a basic ligand such as Py. The intermediate cobalt hydrotricarbonyl is assumed to form a complex with a solvent molecule before it reacts with allyl alcohol, since it is coordinately unsaturated and can, therefore, easily be attacked by surrounding molecules. A basic ligand such as Py (L) is assumed to take part in the reaction by forming complexes (VI) and (VII), since it was proved in a previous study that Py was necessary for the formation of acylcobalt carbonyls.[1]

Acetonitrile forms a complex with metal carbonyls, and, according to Cotton,[9] it possesses a small but real ability to accept π-electrons in competition with CO groups. Accordingly, the complex (I), when S is acetonitrile, will be comparatively stable as a result of π-bonding. The concentration of the complex (II) will, therefore, decrease with an increase in the concentration of acetonitrile as a solvent according to the equilibrium relation (2). Hence, the isomerization, which proceeds *via* the complex (II), will be retarded when acetonitrile is used as a solvent, and the selectivity toward the intramolecular hydroesterification, which can proceed *via* another path, will, relatively, increase; this is in good agreement with the results shown in Table 1. The residue of the analysis shown in Table 1—6, which is an aldolic polymer with a molecular weight of 290,[10] seems to be formed, at least in part, *via* the complex (II), since the selectivity toward the residue decreases together with the selectivity toward propionaldehyde as the amount of acetonitrile increases; however, the exact mechanism of its formation is not known.

The facts that, in the presence of acetonitrile as a solvent, the initial rate increases upon the addition of a small amount of pyridine or another organic base as a ligand (L), and that the selectivity toward γ-butyrolactone in this case increases in proportion to the initial rate (Fig. 2), can be understood by this scheme, for when the step (IV)→(VI) is accelerated by the addition of L, the extent of the isomerization and the polymerization, which are assumed to be independent of the concentration of L, will relatively decrease, and consequently the selectivity toward γ-butyrolactone

---

[8] R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

[9] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

[10] The residue was isolated fom the other products for the determination of the molecular weight and the infrared absorption spectrum.
Molecular weight: 290
IR spectrum: -OH (alcohol), 3420 cm^{-1}
C=O (aldehyde), 1730 cm^{-1}

will increase. The retarding effect of Py on the overall reaction when the Py/$Co_2(CO)_8$ mole ratio exceeds 1 may be due to the formation of pyridinium salt of cobalt hydrocarbonyl, as was proposed in a previous study.[1]

The fact that the selectivity toward isobutyraldehyde increases with an increase in the hydrogen partial pressure is reasonable, since the rate of the hydrogenolysis of VII by hydrogen or $HCo(CO)_4$ will increase with an increase in the hydrogen partial pressure.[11] The hydrogenolysis of VII, therefore, should be the rate-determining step in the isobutyraldehyde formation ; this well accounts for the other experimental fact that the rate of isobutyraldehyde formation is essentially independent of the carbon monoxide partial pressure.

Considering the two equilibrium relations, (1) and (2), it is clear that the larger the carbon monoxide partial pressure, the smaller the concentration of the complex (II) becomes. Hence, the rate of propionaldehyde formation *via* the complex (II) must decrease with an increase in the carbon monoxide partial pressure, while the rate of γ-butyrolactone formation, if it can proceed *via* another path, as is assumed in the scheme, must not be so much retarded by the increase in the carbon monoxide partial pressure. In fact, the results in Table 8 shows that the rate of propionaldehyde formation is retarded by the increase in the carbon monoxide partial pressure to a larger extent than that of γ-butyrolactone formation. Thus, the presence of the two different paths, assumed in the scheme is supported by this fact.

Although it is conceivable that the more stable the complex (II) is made by the choice of the solvent (S), the larger the selectivity toward γ-butyrolactone becomes, no better solvent than acetonitrile has yet been found.

The fact that the effectiveness of solvents in increasing the selectivity toward γ-butyrolactone decreases in the order $CH_3CN > CH_3CH_2CN > (CH_3)_2CHCN > C_6H_5CN$ seems to be related to the concept of HSAB by Pearson *et al.*[12,13] They pointed out that the hardness and, consequently, the electronegativity of the carbonium ion decreases in the order $C_6H_5^+ > (CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3CH_2^+ > CH_3^+$.[13] Accordingly, the softness of the above-mentioned solvents must decrease in the order $CH_3CN > CH_3CH_2CN > (CH_3)_2CHCN > C_6H_5CN$. Hence, according to the principle of HSAB, the complexing ability of these solvents with regard to zero-valent cobalt, which is classified as in the group of soft acids,[12] must decrease in this order. Thus the ability of these solvents (S) to decrease the concentration of complex (II) by means of the equilibrium relation (2) shown in the above scheme and, therefore, their ability to increase the selectivity toward γ-butyrolactone by reducing the rate of isomerization, should decrease in that order also.

A similar effect of nitriles in reducing the isomerization was observed by Roos *et al.*, who studied the effect of nucleophiles on the stoichiometric hydroformylation of 1-pentene.[14]

The author is indebted to Mr. Toshiro Minegishi for his aid in constructing the high-pressure apparatus and to Dr. Ken-ichiro Bando for his discussions.

---

[11] Neither γ-hydroxybutyraldehyde, which may be formed by the hydrogenolysis of VI, nor β-isobutyrolactone, which may be formed by the intramolecular alcoholysis of VII, could be detected in the reaction products; this may be because the intramolecular alcoholysis of VI is very fast, and that of VII, very slow.

[12] R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

[13] R. G. Pearson and J. Songstad, *ibid.*, **89**, 1827 (1967).

[14] L. Roos and M. Orchin, *J. Org. Chem.*, **31**, 3015 (1966).