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Reaction of Cobalt Hydrotetracarbonyl with Acetylene

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The reaction of cobalt hydrotetracarbonyl with acetylene was carried out in methanol as a model of the carboxylation of acetylene. The complexes formed in this reaction were identified by means of IR, NMR, EA and molecular weight measurement. The main product was acetylene dicobalt hexacarbonyl. From the decomposition reaction of this complex in ethanol, ethyl acrylate, ethyl propionate and diethyl succinate were obtained. The yield of ethyl acrylate increased in the presence of carbon monoxide. The reaction course from acetylene to acrylate was examined.

Natta and Pino[1] reported that the carboxylation of acetylene catalyzed by cobaltcarbonyl gives fumaric, acrylic and succinic esters in the presence of hydrogen and carbon monoxide in alcohol. It was found that the rate of acrylate formation is accelerated by the presence of hydrogen.[2] The authors have intended to throw light on the reaction course of carboxylation of acetylene by studying the nature of the complexes obtained from the reaction of cobalt carbonyl with acetylene.

Wender and his colleagues[3] reported that the reaction of cobalt hydrotetracarbonyl with acetylene in gas phase gives propanal and acetylene dicobalt hexacarbonyl. However, the reaction in solutions has not been studied yet.

Reaction of Cobalt Hydrotetracarbonyl with Acetylene. Cobalt carbonyl is known to take the form of hydrotetracarbonyl in alcoholic solution under high pressure of carbon monoxide and hydrogen.[3]

$$Co_2(CO)_8 + H_2 \xrightarrow[ROH]{} 2HCo(CO)_4$$

Thus, the reaction of cobalt hydrotetracarbonyl with acetylene in methanol has been carried out either at −10°C or at 25°C, as a model of the first step of acrylic ester synthesis. In order to compare the reaction products in methanol with those in a non-polar solvent, the same reaction using *n*-hexane as a solvent has also been carried out at −10°C and 25°C.

Triphenylphosphine was added to the reaction mixture. The resulting solution was concentrated and chromatographed on alumina. The products thus isolated are listed in Table 1. Ether-insoluble products I, III, VI and X were identified to be $Co_2(CO)_6[P(C_6H_5)_3]_2$[4a] (I, III, VI) and $[Co(CO)_3$-

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[1] G. Natta, and P. Pino, *Chim. Ind.* (Milan) **1952**, 34, 449.

[2] H. Wakamatsu, J. Sato and M. Takesada, *Shokubai*, **9**, 14 (1967).

[3] I. Wender, H. W. Sternberg, R. A. Friedel, S. J. Metlin and R. E. Markby, " The Chemistry and Catalytic Properties of Cobalt and Iron Carbonyls " (Bureau of Mines Bulletin 600), U. S. Dept. of Interior, Washington, (1962) p. 79.

[4a] O. Vohler, *Chem. Ber.*, **91**, 1235 (1958).

TABLE 1. COMPLEXES OBTAINED FROM THE REACTION OF ACETYLENE WITH COBALT HYDROTETRACARBONYL

Solvent	Reaction temp.	Complex	
Methanol	−10°C	I	$Co_2(CO)_6[P(C_6H_5)_3]_2$
		II	$C_2H_2Co_2(CO)_5P(C_6H_5)_3$
	25°C	III	$Co_2(CO)_6[P(C_6H_5)_3]_2$
		IV	$C_2H_2Co_2(CO)_5P(C_6H_5)_3$
		V	$C_2H_2Co_2(CO)_4[P(C_6H_5)_3]_2$
n-Hexane	−10°C	VI	$Co_2(CO)_6[P(C_6H_5)_3]_2$
		VII	$C_2H_2Co_2(CO)_5P(C_6H_5)_3$
		VIII	$C_2H_2Co_4(CO)_8[P(C_6H_5)_3]_2$
		IX	$HCo(CO)_3P(C_6H_5)_3$
	25°C	X	$[Co(CO)_3(P(C_6H_5)_3)_2]^+[Co(CO)_4]^-$
		XI	$Co_2(CO)_6[P(C_6H_5)_3]_2$
		XII	$C_2H_2Co_2(CO)_5P(C_6H_5)_3$
		XIII	$C_2H_2Co_2(CO)_4[P(C_6H_5)_3]_2$

$(P(C_6H_5)_3)_2]^+[Co(CO)_4]^-$ (X) respectively, based on Vohler's studies.[4b] Complex IX, obtained from the reaction in *n*-hexane, was too unstable to be identified by means of IR and NMR, and rapidly decomposed to $Co_2(CO)_6[P(C_6H_5)_3]_2$. From the color and chemical behavior, complex IX was ascribed to $HCo(CO)_3P(C_6H_5)_3$, which Hieber has already reported.[5] Reddish brown crystals (II, IV, VII and XII) were obtained from the first eluted solution of *n*-hexane. All these components were proved to be identical, and this compound was the main product of the reaction not only in methanol but also in *n*-hexane. This complex shows four strong bands at 2065, 2011, 2001 and 1966 cm^{-1} in terminal carbonyl stretching region of the infrared spectrum. The NMR spectrum shows a doublet at $\delta=-5.03$ and a multiplet at $\delta=-7.3$ in a CS_2 solution. From elemental analysis and molecular weight measurement, the molecular formula was established to be $CH\equiv CHCo_2(CO)_5$-$P(C_6H_5)_3$. The dark green complex (VIII) was obtained from the fraction eluted next to $CH\equiv CHCo_2(CO)_5P(C_6H_5)_3$. Complex VIII shows infrared bands at 2050.0 (s), 2015.0 (s), 1997.0 (m), 1982 (w), 1950 (m) and 1835.0 cm^{-1} in carbonyl stretching region. The NMR spectrum of complex VIII could not be observed, because of low solubility. The elemental analysis and molecular weight measurement have indicated the molecular formula of $C_2H_2Co_4(CO)_8[P(C_6H_5)_3]_2$. For the sake of comparison, the reaction of $Co_4(CO)_{12}$ with acetylene was carried out and the same complex as VIII was obtained.

The final component was isolated and determined to be $CH\equiv CHCo_2(CO)_4[P(C_6H_5)_3]_2$, from the infrared spectrum[6] and elemental analysis. The result is summarized in Table 1. The main product of the reaction of cobalt hydrotetracarbonyl with acetylene was established to be $CH\equiv CHCo_2(CO)_6$ in methanol and in *n*-hexane. The possibility of the association of cobalt hydrotetracarbonyl to form dicobalt octacarbonyl prior to the reaction was excluded for the reaction in methanol, because the former is considerably stable in methanol. The methanol solution of cobalt hydrotetracarbonyl shows only one broad infrared absorption at 1900 cm^{-1}, and this fact indicates that cobalt hydrotetracarbonyl dissociates into H^+ and $Co(CO)_4^-$. The reaction course is suggested as follows:

$$HCo(CO)_4 + CH\equiv CH \rightarrow HCo(CO)_3(CH\equiv CH) + CO$$

$$HCo(CO)_3(CH\equiv CH) + HCo(CO)_4 \rightarrow CH\equiv CHCo_2(CO)_6 + H_2 + CO$$

On the other hand, the reaction of sodium cobalt tetracarbonyl with acetylene has not given $CH\equiv CHCo_2(CO)_6$. This seems to be caused by the stability of $NaCo(CO)_4$ in a methanol solution. It is very interesting that all the complexes obtained from the reaction in methanol have the Co–Co covalent bond.

Decomposition Reaction of Acetylene Dicobalt Hexacarbonyl. Wender and his colleagues have reported that acetylene dicobalt hexacarbonyl catalyzes the polymerization of acetylene.[3] In order to investigate the role of $C_2H_2Co_2(CO)_6$ in acrylic ester formation, the decomposition reaction of this complex was carried out in the presence of ethanol and carbon monoxide.

[4b] W. Hieber and W. Freyer, *ibid.*, **91**, 1230 (1958).

[5] W. Hieber and E. Linder, *Z. Naturforsch.*, *B*, **16**, 137 (1961).

[6] R. F. Heck, *J. Amer. Chem. Soc.*, **85**, 657 (1963).

TABLE 2. PRODUCTS OF DECOMPOSITION REACTION OF $CH{\equiv}CHCo_2(CO)_6$

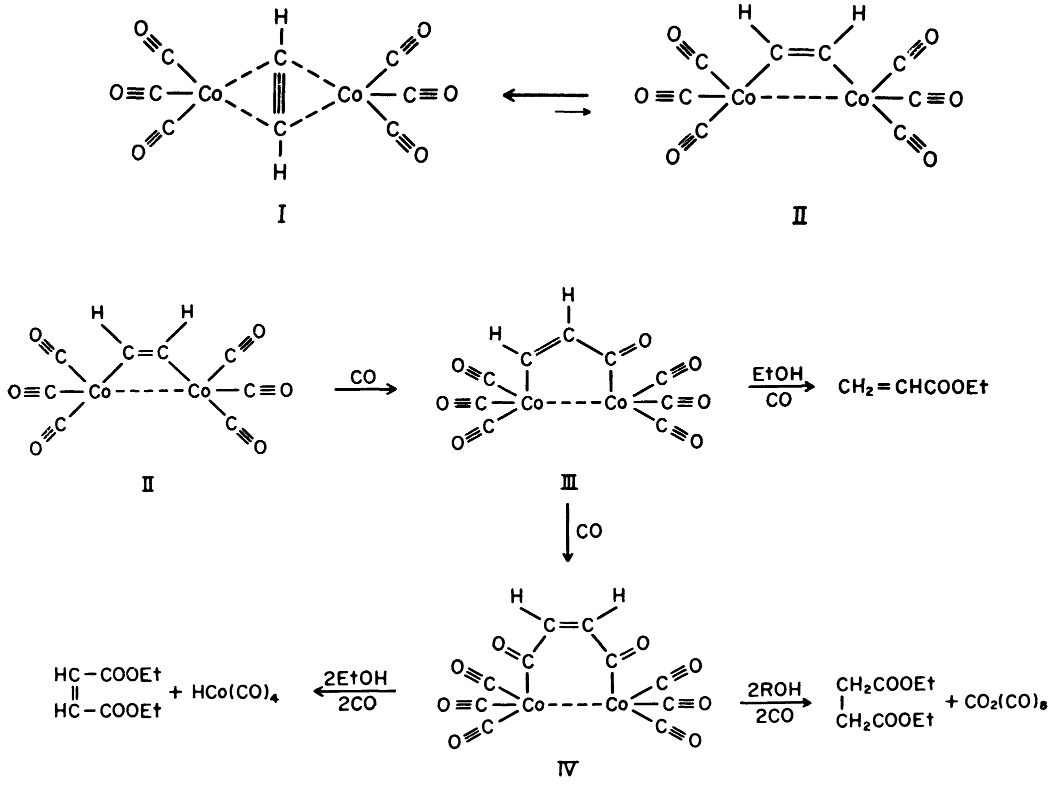
Complex (mM)	Temp. (°C)	CO (kg/cm²)	Time (min)	Ethyl acrylate (%)	Ethyl propionate (%)	Diethyl succinate (%)
2.4	100	101	30	45	5	29
2.6	90	90	300	45	2	49
10.0	100	100	30	34	15	46
1.9	110	110	30	60	2	35
2.0	100	—	10	12	1	—
2.0	100	—	30	6	2	—
2.0	100	—	60	6	5	—
2.0	150	—	30	0	15	—

The reaction products were ethyl acrylate, ethyl propionate and diethyl succinate. In the absence of carbon monoxide the products were ethyl acrylate and ethyl propionate. The results are summarized in Table 2. The principal conclusions which emerge from a scrutiny of these data may be summarized as follows: (1) the presence of carbon monoxide increases the conversion ratio of $C_2H_2Co_2(CO)_6$ to ethyl acrylate, (2) diethyl succinate is not the secondary product from ethyl acrylate but is formed directly from $C_2H_2Co_2(CO)_6$, because the ratio of diethyl succinate to ethyl acrylate is almost constant during the course of reaction. (Table 2)

Reaction Course from Acetylene to Ethyl Acrylate. From the above-described experimental results and discussions, the following scheme can be suggested for the acrylate formation from acetylene under the pressure of carbon monoxide and hydrogen.

$$HC{\equiv}CH + 2HCo(CO)_4 \rightarrow$$
$$HC{\equiv}CHCo_2(CO)_6 + H_2 + 2CO$$
$$HC{\equiv}CH + Co_2(CO)_8 \rightarrow$$
$$HC{\equiv}CHCo_2(CO)_6 + 2CO$$

It has been suggested[7] that coordinated acetylene has C_{2v} symmetry and hybridization of this acetylene



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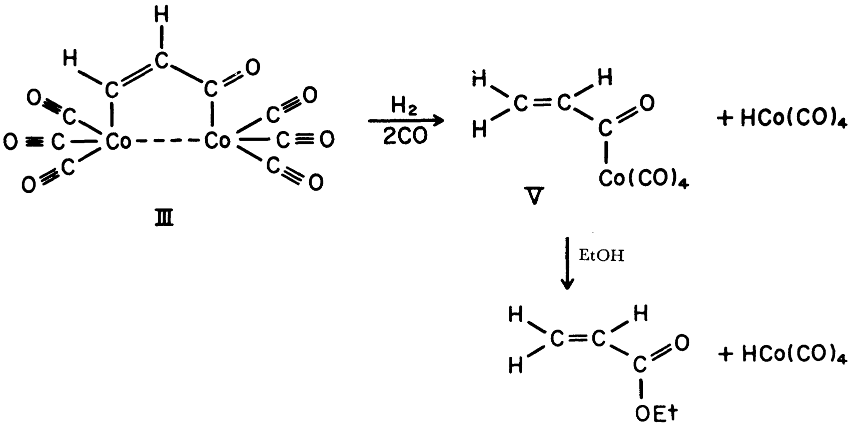
[7] Y. Iwashita, F. Tamura and A. Nakamura, *Inorg. Chem.*, **8**, 1179 (1969).



changes from *sp* to sp^2. The electrons in non-bonding orbital must occupy the two *cis*-positions of ethylene type structure. Therefore, the following isomerization may occur easily during the course of reaction. If the carbon monoxide or another Lewis base attacks isomer (II) the carbon monoxide can be inserted into the carbon-metal bond. This seems similar to the mechanism of butenolactone complex formation proposed by Heck.[8] The formation of other products (fumaric ester[1] and propanal) can be also explained on the basis of these assumed intermediates. Acetylene dicobalt hexacarbonyl has a considerable stability, and therefore, the rate determining step of acrylic ester formation from acetylene should be the transformation of this complex. The cobalt-carbon bond might be split by hydrogen as above. That the hydrogen can accelerate the rate of acrylate formation may be accounted for by these mechanisms.

Experimental

$HCo(CO)_4$ *n*-Hexane Solution. Thirteen grams of $Hg[Co(CO]_4]_2$ was dissolved into 200 m*l* of ether, and 200 g of Na-Hg was added to the solution. The ether solution was condensed after the color of $Hg[Co(CO)_4]_2$ had disappeared. $NaCo(CO)_4$ was obtained as white crystals. Five milliliters of concentrated hydrochloric acid was added to the aqueous $NaCo(CO)_4$ solution, and $HCo(CO)_4$ was extracted by *n*-hexane.

$HCo(CO)_4$ Methanol Solution. $HCo(CO)_4$ was generated from $Co(DMF)_6[Co(CO)_4]_2$ and concentrated HCl, and was absorbed by methanol.

Reaction of Acetylene with $HCo(CO)_4$. Acetylene purified by pyrogallol solution and dried by concentrated H_2SO_4, was admitted into $HCo(CO)_4$ solutions of methanol and *n*-hexane for 3 hr, and 10 g of $P(C_6H_5)_3$ was then added. The reaction mixture was condensed to dryness and extracted by ether. The ether layer was chromatographed on alumina. The main component of the ether soluble products was $C_2H_2Co_2(CO)_5P(C_6H_5)_3$ (yield about 45%). The yields of $C_2H_2Co_2(CO)_4[P(C_6H_5)_3]_2$ and $C_2H_2Co_4(CO)_8[P(C_6H_5)_3]_2$ were 5% and 3%, respectively (25°C, *n*-hexane solution). From ether-insoluble filtrate, $Co_2(CO)_6[P(C_6H_5)_3]_2$ and $[Co(CO)_3(P(C_6H_5)_3)_2]^+[Co(CO)_4]^-$ were obtained, but complete separation of these two species failed because of their sparing solubility in any solvent. (Yields of these two compounds were about 15%.)

Decomposition Reaction of $C_2H_2Co_2(CO)_6$ in Ethanol. $C_2H_2Co_2(CO)_6$ was thermally decomposed in ethanol under the pressure of CO in an autoclave. The reaction mixture was filtered and the filtrate was examined by gas chromatography (column PEG 400 with glycerine).

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[8] R. F. Heck, *J. Amer. Chem. Soc.*, **86**, 2819 (1964).