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The Synthesis of Methacrylic Esters by the Carboxylation Reaction of Methylacetylene. II. Catalytic Synthesis of Methyl Methacrylate using Nickel Carbonyl as the Catalyst

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The catalytic synthesis of methyl methacrylate by the carboxylation reaction of methylacetylene using nickel carbonyl as a catalyst was studied under various conditions. The experimental results concerning the effects of the reaction conditions on the reaction rate, the stability (regeneration) of nickel carbonyl, and the product yields suggested the most desirable conditions for the synthesis. It was ascertained that, in the catalytic process, the pressure of carbon monoxide played a very important roles; a high pressure gave a good regeneration of nickel carbonyl, *i. e.*, a high value of 95% in the so-called catalytic level, but the initial reaction rate decreased remarkably with an increase in the pressure, probably in reverse proportion to its second power, or more. A semicontinuous process was much better for the synthesis than a batch process. A good yield of 85% (based on the methylacetylene used) of the total of methyl methacrylate and methacrylic acid and a high catalytic level of 95% were obtained when the reaction was carried out semicontinuously in the presence of methacrylic acid and water at a total pressure of 13 atm (initial charge of carbon monoxide at room temp.: 4 atm) at 130°C. A mechanism for the catalytic reaction was proposed to account for the experimental results.

In a previous paper,[1)] it has been reported that methylacetylene was more difficult to carboxylate than acetylene and that methyl methacrylate was obtained in unsatisfactory yields under the carboxylation conditions studied. It was also observed that, in the catalytic process using nickel carbonyl as a catalyst, the pressure of carbon monoxide appeared to play a very important role and that water acted as an accelerator of the reaction, as do mineral acids as well known.

The present paper will describe a further investigation of the catalytic synthesis of methyl methacrylate from methylacetylene and carbon monoxide, using nickel carbonyl as a catalyst. The effects of the reaction conditions on the reaction rate, the stability of nickel carbonyl, and the product yields will be examined in order to determine the most suitable conditions for this synthesis and in order to obtain useful information about the carboxylation reaction. Special attention will be paid to the stability (regeneration) of the nickel carbonyl catalyst. A mechanism for the carboxylation reaction will be proposed to account for the experimental results.

Experimental

Materials. Commercial methylacetylene was purified by fractional distillation through a Podbielniak-type low-temperature column (80 cm × 1.5 cm); bp −23—−22°C. The purity was higher than 98.5 mol% on gas chromatographic analysis. Commercial carbon monoxide (99.7 mol% pure) was used. Nickel carbonyl was prepared by the usual method[2)]; bp 42—43°C (lit. 43°C).

Apparatus and Procedures. Two reaction processes were employed.

1) Batch Process. This process was favored over the semicontinuous process for collecting the kinetic data of the reaction. The general procedure was as follows. A 350 m*l* shaking-type stainless-steel autoclave (shaking speed: 240 times per min) was charged with methanol, additives such as water and/or acids, hydroquinone, and a catalytic amount of nickel carbonyl under nitrogen. The vessel was then cooled to about −50°C and evacuated, and the air was completely replaced by nitrogen. Carbon monoxide was introduced to give the specified pressures. Then the vessel was heated to the reaction temperature, at which temperature all the methylacetylene was injected at once through a pipe-line from an injection pump.*[3] After the lapse of an introduction period, the absorption of carbon monoxide was observed; in most cases, the reaction was continued until the absorption had practically ceased. During the reaction period, the total reaction pressure was

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1) Y. Sakakibara, This Bulletin, **37**, 1601 (1964).

*[3] By means of an injection pump manufactured by the Tokyo Koatsu Co., liquefied methylacetylene was njected all at once through a handling operation or ntroduced at a constant rate of 0.5—17 m*l*/hr mechanically.

kept constant by introducing carbon monoxide continuously from a 120 m*l* carbon monoxide-pressure storage tank. The amount of carbon monoxide introduced was calculated from the pressure drop in the pressure storage. After the reaction had been completed, the autoclave was cooled and the reaction mixture was analyzed.

2) Semicontinuous Process. A 200 m*l* rotational-stirring-type stainless-steel autoclave (used at about 900 rpm) was used as the reaction vessel. This process was the same as the above batch process except that methylacetylene was added continuously at the reaction temperature using the injection pump. The addition of methylacetylene was made by first introducing a small portion (0.5—0.8 g of it) quickly; after the reaction had started, the residual portion was added continuously at a moderate rate.

Analytical Procedures. The decomposed and, in several cases, undecomposed nickel carbonyl was analyzed to determine the catalytic level of nickel carbonyl; the catalytic level is expressed as the ratio of the product (ester, carbonic acid) carbonyl coming from gaseous carbon monoxide to the total available carbon monoxide, including that from the nickel carbonyl decomposed. The undecomposed nickel carbonyl was thoroughly removed from the reaction mixture after the gas remaining in the autoclave had been vented off, first by passing nitrogen through the vessel under a slight heating or under stirring, and then by bubbling nitrogen into the reaction mixture in a flask at about 50°C. All of these gases were passed through a mixture consisting of carbon tetrachloride, bromine, and water to decompose the nickel carbonyl, and the nickel was analyzed by the dimethylglyoxime method.3) The decomposed nickel carbonyl was determined by analyzing the nickel in the aqueous layer coming from the extraction procedure described below.

The reaction products, esters and acetone, were determined by gas chromatography using a 2.5 m column of 25% polyethylene glycol 1000 and a 2.4 m column of 25% squalane at 70°C. Toluene was used as the internal standard substance. Carboxylic acids in the reaction mixture were titrated with a sodium hydroxide solution and were regarded as methacrylic acid because gas chromatographic analysis showed that the acids mainly consisted of methacrylic acid.1) Furthermore, the yield of methacrylic acid given assumes that all the nickel resulting from the decomposed nickel carbonyl exists as nickel methacrylate. The remaining reaction mixture was poured into dilute sulfuric acid and extracted with methylene chloride. The aqueous layer was thus provided for the determination of the decomposed nickel carbonyl. The extract was condensed and flash-distilled under reduced pressure.

Results and Discussion

The experimental results for the batch and the semicontinuous process are shown in Tables 1 and 2.

The Effect of Reaction Conditions on the Reaction Rate. In order to examine the effect of reaction conditions on the reaction rate, the experiments were carried out by the batch process at a temperature regulated to about ±2°C (Table 1, Exps. 1—11). Concerning the reaction conditions, such conditions as that the catalytic level was over 90% were examined in order to obtain kinetic data about the catalytic reaction. Under the specified conditions, the reaction began after a short induction period and then proceeded smoothly and catalytically. In these cases, the resulting reaction mixture was a transparent yellow-green liquid without any precipitate. The absorption curves of carbon monoxide under various conditions, listed in Exps. 1—11 of Table 1, are shown in Figs. 1—5. In these figures, the absorption amount has been roughly corrected by taking into account the facts that the partial pressure of methylacetylene in the gas phase of the autoclave decreases with the progress of the reaction and that, as a result, carbon monoxide enters into the autoclave to compensate for the decrease. On the assumption that the partial pressure of methylacetylene is proportional to the total methylacetylene and that the partial pressure is zero at the 90% absorption of the theoretical amount of carbon monoxide, the following correction factor, f, was introduced:

The corrected absorption amount = The apparent absorption amount $\times f$

$$f = V_t \times 0.9/(V_t \times 0.9 + V_v \cdot P)$$

where V_t is the theoretical absorption amount of carbon monoxide; V_v, the volume of the vacant part of the autoclave; and P, the partial pressure of methylacetylene at the start of the reaction, being about 9 atm at 170°C and 10.5 atm at 180°C. The relative initial reaction rates were calculated roughly from the absorption curve of carbon monoxide.

The Effect of the Temperature. The reaction rate is quite sensitive to the temperature, as is shown in Fig. 1. Increasing the temperature from 170

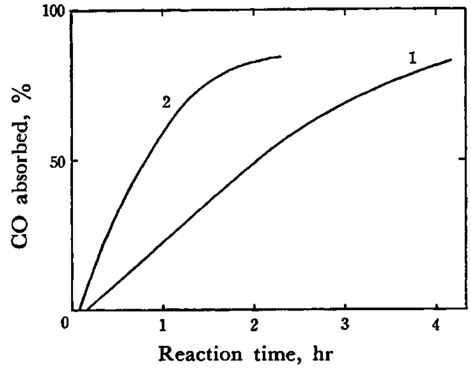

Fig. 1. CO absorption *vs.* time plots for the reaction—Effect of reaction temperature.
Curve number corresponds with Exp. No. in Table 1. Curve 1: 170°C, Curve 2: 180°C

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2) W. Reppe *et al.*, *Ann.*, **582**, 116 (1953).

3) E. R. H. Jones, T. Y. Shen and M. C. Whiting, *J. Chem. Soc.*, **1951**, 766.

TABLE 1. EXPERIMENTAL AND ANALYTICAL DATA FOR BATCH PROCESS

Hydroquinone, 0.1 g

Exp. No.	C_3H_4 g	CH_3OH m*l*	$Ni(CO)_4$ g	Additive		CO		Reaction temp. °C	Reaction time hr	Product[c]				Decomposed $Ni(CO)_4$ %	Catalytic level %
				H_2O m*l*	Acid g	Pressure[a] atm	Absorption amount[b] %			MMA %	MAA %	MC %	Rd g		
1	8.1	70	2.0	10	None	10(45)	83	169—171	4.2	57.7	15.3	6.4	1.3	43	89
2	8.1	70	2.0	10	None	10(53)	84	180—181	2.3	62.3	12.1	7.3	0.8	21	94
3	8.1	70	2.0	10	None	12(55)	83	180—181	2.7	56.5	11.6	6.5	1.1	20	95
4	8.1	70	2.0	10	None	14(58)	70	178—184	3.8	52.6	9.5	5.8	1.4	26	92
5	8.1	70	1.3	10	None	10(53)	73	179—181	2.8	56.5	11.5	6.3	1.0	30	94
6	8.1	70	1.0	10	None	10(53)	66	179—181	4.5	53.0	13.9	5.7	0.5	46	93
7	4.0	70	2.0	10	None	10(45)	75	169—172	3.5	52.7	11.6	5.9	1.0	11	94
8	8.1	63	2.0	18	None	10(45)	83	169—172	2.7	51.2	20.8	5.4	1.2	34	91
9	8.1	70	2.0	10	MAA 0.5	10(45)	77	170—172	2.0	60.7	10.9	5.4	1.0	39	90
10	8.1	70	2.0	10	MAA 1.0	10(44)	77	169—171	1.5	45.0	10.0	4.5	1.3	18	95
11	8.1	70	2.0	10	IBA[d] 1.0	10(45)	61	169—171	1.7	48.8	—	5.9	—	28	91
12	8.7	140	2.0	10	None	5.5(31—26)	82	158—161	3.0	62.7	11.9	7.4	1.5	26(70)[e]	94
13	8.6	120	2.0	35	MAA 5.0	4.5(18—16)	81	125—135	7.0	61.4	17.3	3.9	0.8	35(60)	92

a) The initial pressure of carbon monoxide at room temperature is shown. The values in parentheses show the total pressure at reaction temperature.

b) Expressed as percentage of the theoretical amount based on the methylacetylene used.

c) MMA=methyl methacrylate, MAA=methacrylic acid, MC=methyl crotonate (*trans*), Rd=residue (high boiling materials of bp 60—100°C/50 mmHg, consisting of methacrylic acid mainly, were distilled off.) The yields were calculated on the basis of the methylacetylene used. In Exps. 9, 10, and 13, the yields were given in taking account of the methacrylic acid added.

d) IBA=isobutyric acid e) The values in parentheses show the percentage of the undecomposed nickel carbonyl.

TABLE 2. EXPERIMENTAL AND ANALYTICAL DATA FOR SEMICONTINUOUS PROCESS*

Methanol, 50 m*l*; nickel carbonyl, 2.0 g; hydroquinone, 0.1 g

Exp. No.	C_3H_4 g	Additive		CO		Reaction temp. °C	Reaction time[a] hr	Product				Decomposed $Ni(CO)_4$ %	Catalytic level %
		H_2O m*l*	MAA g	Pressure atm	Absorption amount %			MMA %	MAA %	MC %	Rd g		
14	15.7	7	2.0	9(25)	86	158—162	2.2(1.8)	67.6	14.3	8.7	1.5	31(53)	96
15	9.9	0	5.0	4(13)	87	129—130	2.8(1.8)	80.2	0	8.1	0.7	24(65)	95
16	9.8	2	5.0	4(13)	88	128—130	3.0(1.9)	80.5	4.2	7.4	0.6	23(66)	95
17	10.0	7	2.0	4(13)	85	130—133	2.4(1.6)	70.1	13.6	6.8	0.6	25(66)	95
18	9.9	12	3.0	4(12)	86	128—130	2.5(1.8)	63.2	19.5	5.7	0.8	26(56)	95

* Refer to Footnote a—e in Table 1. a) The values in parentheses show the time of injection of methylacetylene.

to 180°C raised the initial rate by a factor of 3.0. With 160°C, a long induction period of about 1.5 hr was required for the reaction and the rate was very slow.

The Effect of the Pressure of Carbon Monoxide. Increasing the pressure reduces the reaction rate remarkably (Fig. 2). The relative initial rates at 10, 12, and 14 atm pressures (at room temperature) of carbon monoxide were 1.0, 0.6, and 0.3 respectively. From these values, it can roughly be estimated that the initial rate is reversely proportional to the second power of the pressure, or more.

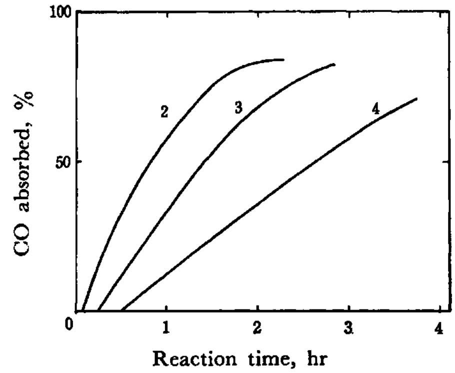

Fig. 2. CO absorption *vs.* time plots for the reaction—Effect of pressure of carbon monoxide.
Curve No.: Exp. No.
Curve 2: 10 atm, Curve 3: 12 atm, Curve 4: 14 atm

In addition, the induction period of the reaction was reduced with a decrease in the pressure, being about 5 min at the 10 atm pressure (Exp. 2).

The Effect of the Amounts of Nickel Carbonyl and Methylacetylene. A decrease in the amount of nickel carbonyl reduces the reaction rate (Fig. 3). The relative initial rates with 2.0, 1.3, and 1.0 g of nickel carbonyl were 1.0, 0.6, and 0.3 respectively.

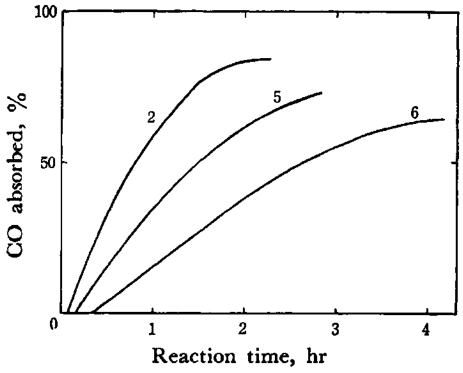

Fig. 3. CO absorption *vs.* time plots for the reaction—Effect of amount of nickel carbonyl.
Curve No.: Exp. No.
Curve 2: 2.0 g, Curve 5: 1.3 g, Curve 6: 1.0 g

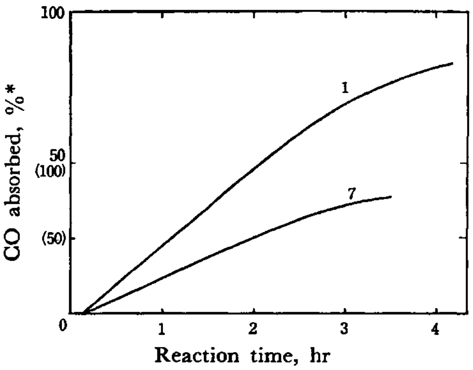

Fig. 4. CO Absorption *vs.* time plots for the reaction—Effect of amount of methylacetylene.
Curve 1: 8.1 g, Curve 7: 4.0 g
* The percentage in parentheses is for Curve 7 in consideration of the absolute amount of carbon monoxide absorbed.

The results suggest that the initial rate might be first-order with respect to the concentration of nickel carbonyl.

Increasing the amount of methylacetylene raises the reaction rate (Fig. 4). The initial rate of Exp. 1, conducted with 8.1 g of methylacetylene, was just twice as fast as that of Exp. 7, with 4.0 g. These results suggest that the initial rate may be first-order also with respect to the concentration of methylacetylene, though the experimental data are yet incomplete.

The Effects of Additives. The reaction did not proceed easily without the addition of certain accelerators; substances with an active hydrogen as inorganic and organic acids and water are known to be effective. Figure 5 and Table 3 show the effects of additives on the reaction rate. Of water, methacrylic acid, isobutyric acid, and hydrogen chloride, hydrogen chloride is the most effective (Exp. 20 in Table 3); the decreasing order of the effect of these additives per mole is

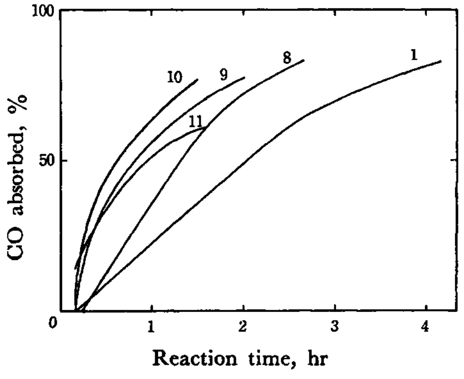

Fig. 5. CO absorption *vs.* time plots for the reaction—Effect of additives.
Curve No.: Exp. No.
See Table 3 concerning the kinds and amounts of additives.

TABLE 3. EFFECT OF ADDITIVES ON REACTION RATE

Exp. No.[a]	Additive		Relative initial rate (Exp. 1=1.0)
	Water		
1	10		1.0
8	18		1.9
	Water + Methacrylic acid		
9	10	0.0	5.9
10	10	1.0	10.2
	Water + Isobutyric acid		
11	10	1.0	(5.0)
	Water + Methacrylic acid		
19[b]	7.0	2.0	1.0[c]
	Water + Hydrogen chloride		
20[b]	7.0	0.9	(7)[c]

a) The Exp. No. corresponds with Exp. No. in Table 1 and Curve No. in Fig. 5.

b) Exps. 19 and 20 were made at 28 atm total pressure (initial charge of carbon monoxide at room temp.: 10 atm) at 130°C with 8.0 g C_3H_4, 50 m*l* CH_3OH, 2.0 g $Ni(CO)_4$, and 0.1 g hydroquinone using the rotational stirring-type autoclave descrived above.

c) These two values were expressed as Exp. 19= 1.0.

as follows: hydrogen chloride > methacrylic acid ≒ isobutyric acid ≫ water. In the use of hydrogen chloride under the conditions studied, however, the reaction rate decreased quite rapidly, probably as a result of the loss of hydrogen chloride by the $CH_3OH + HCl \rightarrow CH_3Cl + H_2O$ reaction. In the case of both water and methacrylic acid, the reaction rate increased with an increase in their amounts. The initial rates were roughly twice as fast when their amounts were doubled (Exps. 1 and 8; Exps. 9 and 10).

A systematic examination of the effect of mixing was not made, though it appeared to be the most important physical variable. Recently,[4] in the catalytic reaction of acetylene under low pressure (total pressure 1.5 atm, usually under atmospheric pressure), it has been reported that the liquid diffusion of carbon monoxide is an important rate step and that it is necessary to keep the liquid diffusion of carbon monoxide rate-controlling in order to maintain the reaction. For obtaining most of the kinetic data, however, it is best to keep the chemical variables rate-controlling. Judging from the above results concerning the effects of certain variables on the reaction rate, the chemical reaction rate appeared to be rate-controlling under the conditions studied.

The Regeneration of Nickel Carbonyl (Catalytic Level). Concerning the catalytic level of nickel carbonyl in the catalytic carboxylation reaction, very little has been known except for the information on the low-pressure catalytic reaction of acetylene.[5] Recently, with acetylene, it has been reported by Ehrreich *et al.*[4] that a catalytic level of 85% at the maximum, and usually 70—80%, was obtained in the low-pressure process by controlling the material-feed rates accurately under certain conditions. Furthermore, they have pointed out that the maximum catalytic levels for the reaction of substituted acetylenes were much less than that for unsubstituted acetylene, though no details were given.

A high pressure of carbon monoxide was necessary for obtaining a high catalytic level, though the high pressure reduced the reaction rate: in practice, a pressure of about 10 atm (at room temperature) was used at 170°C and one of about 4 atm, at 130°C. Consequently, even in the batch method, catalytic levels higher than 90% were obtained easily (Table 1). In the semicontinuous method, the catalytic levels were all above 95% (Table 2). The carbon monoxide pressure in these experiments might be high enough to produce such catalytic levels, though the critical limits of carbon monoxide pressure have not been clarified. On the other hand, even if the apparent pressure of carbon monoxide was high, the catalytic levels were low in cases of either an insufficient mixing of the reactants or the occurrence of a temporary violent reaction. In the batch method especially it was necessary to choose the reaction conditions so that no violent reaction occurred in the early stage of the reaction.

By-products. Methyl crotonate, methyl isobutyrate, and acetone were found as the main by-products, besides the polymerization products of methylacetylene and/or methyl methacrylate formed.[1] Of these by-products, methyl crotonate was measured in largest quantities, especially at higher reaction temperatures. This amount

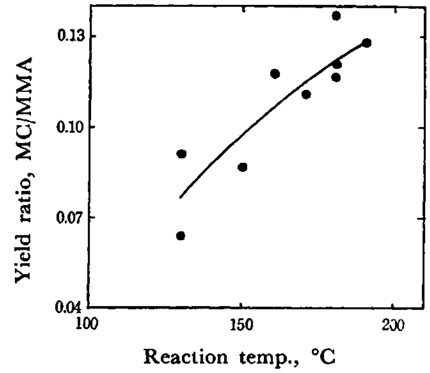

Fig. 6. Yield ratio of methyl crotonate to methyl methacrylate against reaction temp.

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[4] J. E. Ehrreich, R. G. Nickerson and C. E. Ziegler, *Ind. Eng. Chem. Process Design Develop.*, **4**, 77 (1965).

[5] M. Salkind, E. H. Riddle and R. W. Keefer, *Ind. Eng. Chem.*, **51**, 1328 (1959); Numerous patents.

decreased, however, with a decrease in the reaction temperature and the yield ratio of methyl crotonate to methyl methacrylate dropped from about 0.13 at 190°C to about 0.08 at 130°C, as Fig. 6 shows. The amount of methyl isobutyrate was very small (below 0.2%), in most cases being only a trace, in the catalytic reactions conducted at high catalytic levels, as was to be expected from the very small decomposition of nickel carbonyl. Acetone also was found in only a trace under those conditions.

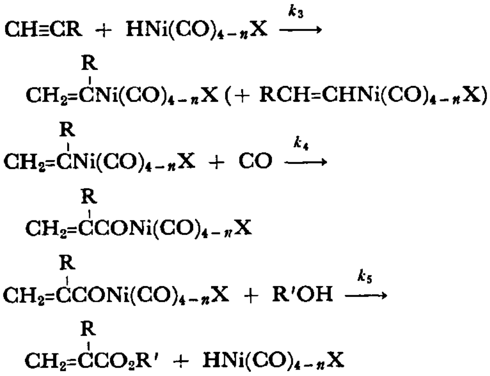
Although the loss of methylacetylene due to its polymerization appeared to be a main cause of the poor yield of the carboxylation products in the batch method, as has been described in the previous paper,1) the polymerization was markedly decreased by adding methylacetylene continuously and by carrying out the reaction at a low temperature (Table 2).

Optimum Conditions for the Synthesis of Methyl Methacrylate. The above results concerning the reaction rate, the catalytic level, and the by-products in the catalytic reaction give some hints for a search after the optimum conditions for this synthesis, though their determination is difficult. As expected, it would be advantageous to carry out this reaction under the following conditions: at as low and constant a pressure as possible, in order to make the reaction rate fast, within the critical limits for maintaining high catalytic levels; at as low and constant a temperature as possible, to suppress the formation of methyl crotonate, taking account of the reaction rate; in the presence of such effective additives as acids and water; under a mixing sufficient to keep the liquid diffusion of carbon monoxide good; and by a continuous process, to suppress the polymerization of methylacetylene and methyl methacrylate and to avoid a temporary violent reaction.

Therefore, the synthesis was attempted semicontinuously using a laboratory apparatus by which at least methylacetylene and carbon monoxide were each introduced continuously, though it would be better to feed all the raw materials continuously under accurate control. Several results are shown in Table 2. Under the present conditions, the catalytic reaction began a short time after the addition of a small amount (0.5—0.8 g) of methylacetylene, and thence proceeded smoothly at a high catalytic level, over 95%. The total yield of methyl methacrylate and methacrylic acid was 82—85%. The best yield, 85%, was obtained when the reaction was carried out in the presence of methacrylic acid and a small amount of water at a total pressure of 13 atm (initial charge of carbon monoxide at room temperature: 4 atm), a reaction temperature of 130°C, and a feed rate of 4.8 g/hr (Exp. 16). The use of a lower carbon monoxide pressure is promising and would possibly be more advantageous. With a lower pressure, however, it was difficult to control and maintain the catalytic reaction using our apparatus, because the effect of the fluctuation of the carbon monoxide pressure on the reaction rate and the catalytic level becomes remarkably large with a decrease in the pressure. Recently, Happel *et al.*6) have reported the synthesis of methyl methacrylate by a low pressure catalytic carbon monoxide-nickel carbonyl-methylacetylene process, as used with acetylene itself. The catalytic level, however, seems to be lower than 70%.

Reaction Mechanism. The mechanism of the catalytic carboxylation reaction has not yet been well clarified though it has been discussed by several workers.7) On the basis of our experimental results, the following mechanism, similar to one of the possible mechanisms presented by Heck,7a) may be proposed:

$$\mathrm{Ni(CO)_4 + HX \underset{k_2}{\overset{k_1}{\rightleftarrows}} HNi(CO)_{4-n}X + \mathit{n}CO} \qquad (1)$$



$$\mathrm{CH{\equiv}CR + HNi(CO)_{4-n}X \xrightarrow{k_3} CH_2{=}\overset{R}{C}Ni(CO)_{4-n}X\ (+\ RCH{=}CHNi(CO)_{4-n}X)} \qquad (2)$$

$$\mathrm{CH_2{=}\overset{R}{C}Ni(CO)_{4-n}X + CO \xrightarrow{k_4} CH_2{=}\overset{R}{C}CONi(CO)_{4-n}X} \qquad (3)$$

$$\mathrm{CH_2{=}\overset{R}{C}CONi(CO)_{4-n}X + R'OH \xrightarrow{k_5} CH_2{=}\overset{R}{C}CO_2R' + HNi(CO)_{4-n}X} \qquad (4)$$

HX = water, organic or inorganic acids
R′ = H or alkyls

Assuming that reaction (1) is a rapid reversible reaction and that reaction (2) is the rate-determining step, which is followed by the two rapid reactions, (3) and (4), the initial rate of the overall reaction can be given by the following equation:

$$\text{Initial rate} = (k_1k_3/k_2)[\mathrm{Ni(CO)_4}][\mathrm{HX}][\mathrm{RC{\equiv}CH}]/(P_{\mathrm{CO}})^n$$

The experimental results concerning the initial reaction rate seem to confirm the above relationship, though they are rough.

Reaction (1) forms a hydronickel carbonyl hydroxide ($\mathrm{HNi(CO)_{4-n}X}$, X=OH), which is the true catalyst. This reaction (1) is supported by the experimental finding that the reaction rate was accelerated by the presence of such additives as water and acids, and markedly decreased with an increase in the carbon monoxide pressure.

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6) J. Happel and C. J. Marsel, Belg. Pat. 639260 (1964) (*Chem. Abstr.*, **62**, 9019 (1965)).

7) a) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 2013 (1963); b) C. W. Bird, *Chem. Revs.*, **62**, 283 (1962); c) P. L. Pauson, *Proc. Chem. Soc.*, **1960**, 297.

Furthermore, effective additives may be supposed to form a highly reactive $HNi(CO)_{4-n}X$. The n value in $HNi(CO)_{4-n}X$ would probably be 2 or higher, in view of the fact that the initial rate is reversely proportional to over the second power of the carbon monoxide pressure. The subsequent steps, reactions (2)—(4), are similar to those proposed to explain the hydroformylation reaction,[8] except for replacing hydrogen reduction with hydrolysis or alcoholysis. In addition, judging from the distribution of the reaction products, it may be concluded that, under the conditions studied, reaction (2) proceeds predominantly to give an addition product, alkenylnickel carbonyl hydroxide (X=OH), with a branched chain.

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8) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961); J. A. Bertrand, C. L. Aldridge, S. Husebye and H. B. Jonassen, *J. Org. Chem.*, **29**, 790 (1964).