*The Synthesis of Methacrylic Esters by Carboxylation Reaction of Methylacetylene. I. Methyl Methacrylate; Reaction Conditions and Products**

By Yasumasa SAKAKIBARA

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In previous papers[1,2] the present author has reported the synthesis of methylacetylene by the pyrolysis of propylene. In this connection, it is of great interest to synthesize methacrylic esters, especially methyl methacrylate, by the carboxylation reaction of methylacetylene.

Numerous investigations have been made of the synthesis of acrylic esters by the carboxylation of acetylene;[3] the following three processes are known:

The stoichiometric process

$$4CH{\equiv}CH+Ni(CO)_4+4ROH+2HCl \rightarrow$$
$$4CH_2{=}CHCO_2R+NiCl_2+H_2$$

The catalytic process

$$CH{\equiv}CH+CO+ROH \xrightarrow{\text{Catalyst}} CH_2{=}CHCO_2R$$

Catalyst: Nickel halides, triphenylphosphine nickel complexes, etc.

The semicatalytic process**

The stoichiometric process plus

$$CH{\equiv}CH+CO+ROH \xrightarrow{Ni(CO)_4} CH_2{=}CHCO_2R$$

Concerning the carboxylation of methylacetylene, however, very little has been published. One article by Yakubovich and Volkova[4] and one patent[5] have described the synthesis of methacrylic acid and its lower alkyl esters by the stoichiometric process (low yields). Recently, it has been reported by another patent[6] that aminoalkyl methacrylates were synthesized in fairly good yields from methylacetylene by the semicatalytic process. Jones et al.,[7] investigating the carboxylation of various monosubstituted acetylenes by the stoichiometric process, obtained ethyl α-butylacrylate in a 50% yield from butylacetylene. This paper will describe the synthesis of methyl methacrylate by the carboxylation reaction of methylacetylene. In this investigation the reaction will be examined by both the stoichiometric and catalytic, including the semicatalytic, processes.

Experimental

Materials. — Methylacetylene was prepared by the dehydrobromination of propylene bromide with potassium hydroxide.[8] The crude methylacetylene was purified by fractional distillation through a Podbielniak-type low-temperature column (80 cm. × 1.5 cm.); b. p. $-23\sim-22$°C. The purity was higher than 98.5 mol.%; allene was shown to be the principal impurity by gas chromatographic analysis.

Carbon monoxide (99.7 mol.% pure) was purchased from the Takachiho Chemical Co.

Metal Carbonyls. — Nickel tetracarbonyl,[9] chromium hexacarbonyl,[10] and dicobalt octacarbonyl[11] were prepared by the usual methods.

Nickel tetracarbonyl: a colorless, transparent liquid; b. p. 42~43°C (lit. 43°C).

Chromium hexacarbonyl: colorless crystals; m. p. 153~155°C (lit. 152~155°C).

Dicobalt octacarbonyl: dark-brown crystals; m. p. 51°C (lit. 51°C).

Nickel Halides and Triphenylphosphine Nickel Bromide Complexes.—Anhydrous nickel bromide and

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1) Y. Sakakibara, This Bulletin, 37, 1262 (1964).

2) Y. Sakakibara, ibid., 37, 1268 (1964).

3) a) J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York (1949), p. 246; b) W. Reppe, *Ann.*, **582**, 1 (1953); c) K. Ohashi, S. Suzuki, H. Ito, M. Yonezawa and K.Ueno, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zassi)*, **55**, 120, 607, 718 (1952); d) M. Maki, *J. Fuel Soc. Japan*, **32**, 410, 414 (1953); e) K. Yamamoto, K. Sato and M. Oku, This Bulletin, **27**, 491 (I-VI) (1954); f) M. Salkind, E. H. Riddle and R. W. Keefer, *Ind. Eng. Chem.*, **51**, 1328 (1959); Numerous patents.

** This process is a modification of Reppe's stoichiometric reaction: a catalytic reaction of carbon monoxide, acetylene, and alcohol by nickel carbonyl is superimposed upon the stoichiometric reaction (See Ref. 3f). In this paper, this process is classified as a catalytic process.

4) A. Ya. Yakubovich and E. V. Volkova, *Doklady Akad. Nauk S.S.S.R.*, **84**, 1183 (1952); (*Chem. Abstr.*, **47**, 3278 (1953)).

5) National Lead Co., Brit. Pat. 887433 (1962); (*Chem. Abstr.*, **57**, 11027 (1962)).

6) N. T. Gehshan and E. H. Specht, U. S. Pat. 2990403 (1961); (*Chem. Abstr.*, **56**, 9933 (1962)).

7) a) E. R. H. Jones, T. Y. Shen and M. C. Whiting, *J. Chem. Soc.*, **1950**, 230; b) **1951**, 766.

8) G. B. Heisig and H. M. Davis, *J. Am. Chem. Soc.*, **57**, 339 (1935).

9) W. Reppe and coworkers, *Ann.*, **582**, 116 (1953).

10) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart (1954), p. 1340; B. B. Owen, J. English, Jr., H. G. Cassidy and C. V. Dundon, *J. Am. Chem. Soc.*, **69**, 1723 (1947).

11) A. A. Blanchard and P. Gilmont, ibid., **62**, 1192 (1940).

nickel iodide were prepared by drying their hydrates at 140°C.[12]

Bis(triphenylphosphine)nickel dibromide, $(Ph_3P)_2NiBr_2$, was prepared by Yamamoto's procedure.[3e] It was a deep green solid; m. p. 218∼220°C (lit. 221∼222°C) (Found: C, 58.57; H, 4.31%).

Bis(triphenylphosphine)nickel dibromide *n*-butyl bromide, $(Ph_3P_2)_2NiBr_2BuBr$, was prepared by Reppe's procedure.[13] It was a bluish green solid; m. p. 178°C (lit. 178°C) (Found: C, 54.62; H, 4.71%).

Carboxylation. — *Stoichiometric Process.* — Two methods were employed. A) In a 200 ml., four-necked flask equipped with a mercury-sealed stirrer, a gas inlet, a dropping funnel, a thermometer, and a reflux condenser, methanol, concentrated hydrochloric acid, and hydroquinone were placed. The condenser was the same one as that of Jones et al.[14] and contained a mixture of dry ice - ethanol kept at about −20°C. The air in the flask was replaced completely by nitrogen while the flask was heated on a water bath. About 1 ml. of nickel carbonyl was added, and methylacetylene or a gas mixture of methylacetylene and acetylene was bubbled continuously through the solution while it was vigorously stirred. When the reaction began, as shown by a rise in the temperature and, in some cases, by a transient brown coloration, the remainder of the nickel carbonyl was added drop by drop at such a rate that the temperature remained constant. After dropping all amounts of nickel carbonyl, gas was introduced until the absorption stopped practically.

B) A 100 ml. electromagnetic stirring-type autoclave was charged with methanol, concentrated hydrochloric acid, nickel carbonyl, and hydroquinone. The vessel was then cooled to about −40°C and the air was replaced completely by nitrogen. After evacuation, methylacetylene was added by distillation. The vessel was heated slowly to about 80°C, at which temperature a vigorous reaction began; when a marked rise in the temperature was observed, the heating was stopped or weakened. After the mixture had cooled to room temperature, the remaining gas was discharged and collected in a gas holder for the analysis.

Catalytic Process. — A 100 ml. electromagnetic stirring-type autoclave was charged with methanol, a catalyst, hydroquinone, and methylacetylene in the same manner as in the above Process-B. Carbon monoxide was added to give a pressure of 15∼25 atm. in most cases. The vessel was then heated to 150∼290°C. During the period of reaction, when the partial pressure of carbon monoxide fell to about 10 atm. (at 170°C, about a 30 atm. pressure resulted from a mixture of methanol (20 ml.) and methylacetylene (8 g.)), carbon monoxide was added repeatedly to maintain a partial pressure of 10∼40 atm. at the reaction temperature. In most cases, the reaction was continued until the absorption of carbon monoxide stopped practically. After the mixture had cooled to room temperature, the remaining gas was discharged through two traps cooled with ice-water (trap 1) and with dry ice - ethanol (−60°C, trap 2). The condensate in trap 2 was composed mainly of methyl ether and unreacted methylacetylene.

The Separation and Identification of Reaction Products.—*Waste Gases.* — These were analyzed by gas chromatography using the following three different columns: (1) a molecular sieve 5A column (2.4 m.) for hydrogen, nitrogen, methane, and carbon monoxide at 60°C, (2) a 30% (by weight) dioctyl phthalate column (4.7 m.) at room temperature, and (3) an 8.0% β, β'-oxydipropionitrile on silica gel column (2.5 m.) at 70°C for other gaseous substances.

Nickel Carbonyl.—In several cases, the nickel carbonyl, unchanged or formed from nickel-containing catalysts, was determined by a slight modification of the method of Jones et al.[7b]

Liquid Products.—The reaction mixture was poured into dilute sulfuric acid and extracted with methylene chloride. Acetone and esters were determined by gas chromatographic analysis of the extract. Two columns, a 2.4 m. column of 23% β, β'-oxydipropionitrile and a 2.4 m. column of 25% squalane, were used at 70°C, with a flow rate of 50 ml./min. of hydrogen as a carrier gas; *p*-xylene and toluene were selected as the internal standard substances respectively. The retention times measured under these conditions are shown in Table I.

TABLE I. RETENTION TIMES

Compound	Retention time, min.	
	β, β'-Oxydipropionitrile	Squalane
Methylene chloride	4.9	2.5
Methanol	7.3	1.0
Acetone	8.5	1.8
Methyl isobutyrate	8.7	8.9
Methyl propionate	9.1	5.5
Methyl acrylate	10.4	4.9
Methyl *n*-butyrate	14.6	12.6
Toluene	14.7	26.3
Methyl methacrylate	14.9	11.5
Water	17.2	2.0
p-Xylene	24.0	64.8
Methyl *trans*-crotonate	33.8	18.2

The above extract was washed thoroughly with a 7% sodium hydrogen carbonate solution, and the neutral and acidic fractions were separated. The alkaline solution was acidified with dilute sulfuric acid and extracted with methylene chloride. This extract was then condensed and flash-distilled at reduced pressure. The distillate was analyzed by gas chromatography to determine the carboxylic acids. The analysis was performed by a 2.4 m. column of 21% dioctyl sebacate +4% sebacic acid[15]

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12) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart (1954), pp. 1155-1157.

13) W. Reppe, French Pat. 961010; (*Chem. Abstr.*, **46**, 5617 (1952)).

14) E. H. Jones, T. Y. Shen and M. C. Whiting, *J. Chem. Soc.*, **1951**, 48.

15) G. Raupp, *Angew. Chem.*, **71**, 284 (1959).

at 140°C, using chlorobenzene as an internal standard substance. On the other hand, the neutral fraction was condensed and flash-distilled at reduced pressure to give an ester fraction (~80°C/150 mmHg), a high-boiling fraction (60~100°C/50 mmHg), and a residue. In most cases of experiments which were carried out by the catalytic process, the extract, without separating the neutral and acidic fractions, was worked up like the above neutral fraction. The high-boiling fraction was analyzed by gas chromatography to determine the carboxylic acids.

By fractionating low-boiling fractions collected from several runs, the following compounds were isolated and identified:

Acetone; b. p. 56~57°C: 2,4-dinitrophenylhydrazone; m. p. 125°C (Found: N, 23.62%).

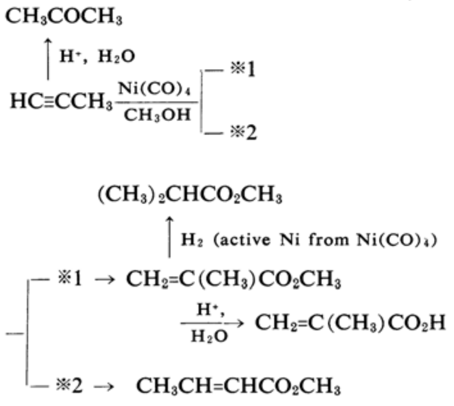
Methyl methacrylate; b. p. 47~48°C/112 mmHg, n_D^{20} 1.4149, d_4^{20} 0.947 (Found: C, 60.04; H, 8.25%).

Methyl *trans*-crotonate; b. p. 57~58°C/84 mmHg, n_D^{20} 1.4248, d_4^{20} 0.944 (Found: C, 59.85; H, 8.36%).

Results and Discussion

Stoichiometric Process.—*Carboxylation under Atmospheric Pressure.*—The carboxylation reaction was performed by introducing methylacetylene into a solution of methanol and concentrated hydrochloric acid with nickel carbonyl. The results are shown in Table II. By this method methylacetylene was not carboxylated so rapidly as acetylene. Even at a temperature of 73~76°C, no obvious reaction occurred, and methyl methacrylate was obtained in only a slight yield (3.6%, based on the methylacetylene consumed); about one half of the methylacetylene was recovered (Run 61). In this run, although the greater part (70%) of the nickel carbonyl used was consumed, most of carbon monoxide resulting from its decomposition was found in the waste gas as free carbon monoxide without having reacted with methylacetylene. When *n*-butanol was used instead of methanol, the reaction appeared to proceed slowly at 72~76°C after an induction period of several minutes, but the yield of butyl methacrylate was low (16%, Run 59). The addition of acetylene accelerated the reaction considerably. When a gas mixture of methylacetylene and acetylene in a 1 to 2 : 1 volume ratio was employed, a vigorous exothermic reaction occurred after a short induction period. The rate of the reaction became slower when the ratio of methylacetylene to acetylene is increased, and in the case of the 3 : 1 ratio, the reaction proceeded slowly under continuous heating (Run 57). In the case of the 2 : 1 ratio, the total yield of methyl methacrylate and methacrylic acid was 45%, the best yield in these three runs (Runs 56−58), while the total yield of methyl acrylate and acrylic acid produced from acetylene was 66%. The total yield of the carboxylation products (monomeric) of methylacetylene was always much lower than that of acetylene, and the residue (expressed as Rd in Table II) increased with an increase in the ratio of methylacetylene in the gas mixture. In view of these results, it is likely that, compared with acetylene, methylacetylene is difficult to carboxylate, but it can be polymerized and/or added to olefinic compounds such as methyl methacrylate, methyl acrylate, etc., under the conditions of the carboxylation reaction.

In addition to methyl methacrylate and methacrylic acid, methyl *trans*-crotonate, methyl isobutyrate, and acetone were obtained from methylacetylene as by-products in small amounts. The routes of formation of these substances are presumed to be as follows:



It should be noted that methyl isobutyrate, formed by the hydrogenation of methyl methacrylate, was obtained in much lower yields than was the methyl propionate formed by the hydrogenation of methyl acrylate, especially in Run 57, where the methylacetylene/acetylene ratio is 3 : 1.

Carboxylation under Pressure. — As the carboxylation reaction of methylacetylene did not proceed smoothly under atmospheric pressure, the reaction was examined by heating the reactants in an autoclave. By this method the carboxylation was achieved readily. The results are shown in Table III. In all cases, when the reaction temperature attained about 80°C a vigorous reaction took place, as was evidenced by a sudden marked rise in the temperature and a fall in the pressure. For example, in Run 16, the reaction temperature rose rapidly from 80 to 105°C, and a maximum pressure, at 14 atm., was reached at 82°C. In Run 63, where an excess of methylacetylene was used, 1.23 times the theoretical amount of methylacetylene (based on the nickel carbonyl used) was absorbed, and methyl

TABLE II. STOICHIOMETRIC PROCESS UNDER ATMOSPHERIC PRESSURE

Methanol, 32 ml.; concd. hydrochloric acid, 20 ml.; hydroquinone, 0.1 g.

Run No.	Acetylene and nickel carbonyl	Reaction temp. °C	Reaction time hr.-min.	Recovered acetylene C_3H_4 l.	Recovered acetylene C_2H_2 l.	Product[a)] From C_3H_4 MMA %	From C_3H_4 MAA %	From C_3H_4 Other product %	From C_2H_2 %	HBM g.	Rd g.
61	C_3H_4 3.55 l. (6.0 g.) $Ni(CO)_4$ 4.8 g.	73～76	4.00	1.61 (2.7 g.)		3.6 (2.7)	Trace	MC Trace MIB 1.2 A 2.1		—	0.8
58	C_3H_4-C_2H_2 1 : 1 12.0 l. (17°C) $Ni(CO)_4$ 17.0 g.	38～48	2.08	0.20	0.24	35.6 (43.6)	3.8 (4.7)	MC 0.4 MIB 0.4 A 0.7	MA 66.8 (80.9) AA 2.3 MP 2.3	4.1	3.7
56	C_3H_4-C_2H_2 2 : 1 11.9 l. $Ni(CO)_4$ 17.6 g.	50～57	3.50	0.99	0.55	40.7 (43.2)	4.0 (4.2)	MC 0.3 MIB 0.7 A 1.8	MA 64.5 (67.3) AA 1.9 MP 8.7	2.8	5.6
57	C_3H_4-C_2H_2 3 : 1 12.3 l. $Ni(CO)_4$ 17.1 g.	54～58	4.30	0.35	0.12	30.0 (37.2)	1.9 (2.4)	MC 0.8 MIB 0.8 A 1.9	MA 45.2 (56.0) AA 1.0 MP 16.8	2.0	7.9
59[b)]	C_3H_4 4.57 l. $Ni(CO)_4$ 7.7 g.	72～76	3.00	0.2		BMA 16.1 (17.1)	1.2 (1.3)	A 4.5			

a) MMA=methyl methacrylate, MAA=methacrylic acid, MC=methyl crotonate (*trans*), MIB=methyl isobutyrate, A=acetone, MA=methyl acrylate, AA=acrylic acid, MP=methyl propionate, HBM=high-boiling materials, Rd=residue. The yields were calculated on the basis of the acetylenes consumed. The values shown in parentheses are the yields based on the nickel carbonyl used, but, in the case of the mixed gas, those based on the amount of the nickel carbonyl divided into two parts in the ratio of methylacetylene to acetylene.

b) Butanol (46 ml.) and concentrated hydrochloric acid (10 ml.) were used. BMA=butyl methacrylate.

TABLE III. STOICHIOMETRIC PROCESS UNDER PRESSURE

Methanol, 30 ml.; concd. hydrochloric acid, 12 ml.; nickel carbonyl, 10.7 g.; hydroquinone, 0.1 g.

Run No.	C_3H_4 g.	$C_3H_4/Ni(CO)_4$ equivalent ratio	Reaction temp. °C	Reaction time min.	Recovered C_3H_4 g.	Product[a)] MMA %	MAA %	MC %	MIB %	A %	HBM g.	Rd g.
16	10.4	1.03	16～ 80 80～105	55 30	Trace	36.8 (38.0)	4.9 (5.1)	0.8 (0.8)	1.2 (1.2)	—	2.9	2.7
63	13.5	1.34 (1.23)[b)]	80～116	40	1.1	44.5 (55.0)	4.9 (6.1)	2.3 (2.8)	0.3 (0.3)	1.7	4.0	1.8
15	14.7	1.46	90～120	90	—	(58.8)	(7.4)	(2.0)	(1.2)	—	3.7	1.3

a) The values shown in parentheses are the yields based on the nickel carbonyl used.

b) This value is the ratio of the amount of methylacetylene absorbed to the theoretical amount based on the nickel carbonyl used.

methacrylate was obtained in a 45% yield, together with methacrylic acid in a 5% yield. On the other hand, the best total yield of methyl methacrylate and methacrylic acid, based on nickel carbonyl, was 66% (Run 15).

In all runs, considerable amounts of high-boiling materials (b. p. 87～92°C/47 mmHg, n_D^{20} 1.4760 in Run 15), in addition to small amounts of methyl crotonate, methyl isobutyrate, and acetone, were obtained as by-products. Although the high-boiling materials appeared to be C_7 olefinic esters formed by the dimerization of methylacetylene and the subsequent carboxylation and/or by the addition of methylacetylene to methyl methacrylate, no further study was made. In the stoichiometric reaction, one mole of hydrogen per mole of nickel carbonyl must be formed, if the reaction formula is correct. In reality, however, most of the hydrogen formed appeared to react with unsaturated substances. For example, in Run 63, only 16% of the theoretical amount of hydrogen was found in the waste gas (1920 ml.) as free (4 ml.) or combined hydrogen, that is, as hydrogen which added to methylacetylene to give propylene (227 ml.), as is shown in Table IV. Furthermore, in view of the fact that the yield of methyl isobutyrate was also small, it may be concluded that most of the hydrogen must be added to unsaturated high-molecular substances. This was observed similarly in Run 57, carried out under atmospheric pressure. In this case, only 7% of the theoretical amount of hydrogen was accounted for by the presence of free or combined hydrogen in the waste gas (Table IV), while 21% and 3% were accounted for by the formation of methyl propionate and methyl isobutyrate respectively.

TABLE IV. COMPOSITION OF WASTE GAS

Run No.	63	57
Total amount, ml.	1920	1600
Composition, vol.%		
Nitrogen	7.6	19.5
Hydrogen	0.2	0.1
Carbon monoxide	25.9	26.7
Ethylene	0.1	1.7
Acetylene	—	7.3
Propylene	11.8	8.2
Allene	0.2	0.2
Methylacetylene	33.5	21.6
Methyl chloride	13.2	8.1
Nickel carbonyl	0.9	3.1
Others	6.6	3.5

Catalytic Process.—*Nickel Halide and Triphenylphosphine Nickel Bromide Complex Catalysts.*—The results are shown in Table V. Generally, in the presence of these catalysts the reaction proceeded fairly smoothly at a temperature of 170～180°C and under about a 10 atm. partial pressure of carbon monoxide, as is illustrated by the variation in total pressure shown in Fig. 1. A high pressure of carbon monoxide gave a slow rate of reaction. For example, in the case of about a 75 atm. partial pressure of carbon monoxide (total pressure, 105 atm.), the decrease in pressure during a reaction time of 10 hr. was only two atms. The induction period appeared to be reduced with the decrease in the partial pressure of carbon monoxide when other conditions were the same.

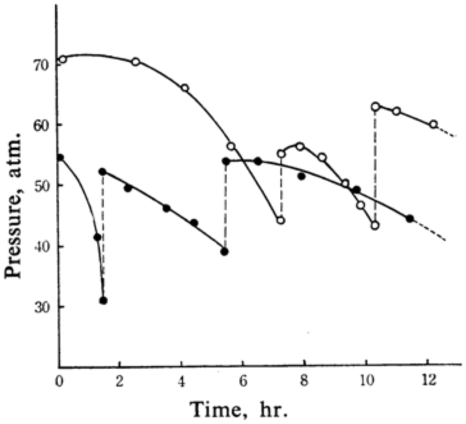


Fig. 1. Variation in total pressure with the reaction time-I*: ●, Run 41; ○, Run 44.
* The vertical broken lines show the added pressure of carbon monoxide.

Triphenylphosphine nickel bromide and triphenylphosphine nickel bromide butyl bromide complexes gave better results than those obtained by nickel bromide and iodide, though these complexes have been reported to decompose with the separation of triphenylphosphine in methanol.[3a,3e] The total yield of methyl methacrylate and methacrylic acid was, however, unsatisfactory (best yield: 47% in Run 44), and a fairly long reaction time was required for the completion of the reaction.

The low yield appeared to be due chiefly to the loss of methylacetylene by polymerization leading to the formation of high-molecular substances (expressed as HBM and Rd in Table V). Particularly, large quantities of high-molecular substances were formed in cases where a vigorous exothermic reaction occurred in the early stages of the reaction, as shown by a marked fall in pressure (Run 41 in Table V and Fig. 1). Such a vigorous reaction was often encountered when the reaction was carried out at a low pressure of carbon monoxide (partial pressure below about 10 atm.) in the presence of the complex catalysts; it was observed that, at that time,

TABLE V. CATALYTIC PROCESS USING NICKEL HALIDES AND TRIPHENYLPHOSPHINE NICKEL BROMIDE COMPLEXES

Hydroquinone, 0.05 g.

Run	C_3H_4	CH_3OH	Catalyst		CO		Reaction temp.	Reaction time	Recoverd C_3H_4	Product[c)					
No.	g.	ml.		g.	Pressure[a) atm.	Absorption amount[b) %	°C	hr.	g.	MMA %	MAA %	MC %	A %	HBM g.	Rd g.
20	8.2	20	$NiBr_2$	1.5	64~39	37	170~175	16.0	0.7	18.0	0.7	2.3	23.5	1.1	3.5
19	6.3	15	$NiBr_2$ CH_3J	1.5 0.13	75~38	71	(150~153 168~173	4.0) 36	0	29.3	(unreacted) —	5.1	18.6	1.5	2.4
18	5.0	15	NiJ_2	2.0	58~31	93	168~174	9.8	—	24.8	2.8	4.8	6.9	1.5	2.8
41	8.4	20	$(Ph_3P)_2NiBr_2$	1.4	57~31	40	170~175	19.6	0.2	18.0	1.1	3.4	2.6	0.8	6.5
36	7.6	20	$(Ph_3P)_2NiBr_2$	1.4	63~36	60	170~175	16.4	0.3	38.9	1.9	7.2	2.8	1.1	3.6
44	8.0	20	$(Ph_3P)_2NiBr_2$	1.4	71~40	58	170~175	21.5	0.3	44.2	2.4	8.3	3.6	0.7	3.8
42	7.1	20	$(Ph_3P)_2NiBr_2$-C_4H_9Br	1.7	57~38	53	170~175	19.7	0.1	36.0	2.0	6.5	6.9	0.7	4.5
35	8.4	20	Ph_3P $NiBr_2$ C_4H_9Br	1.0 0.4 0.5	59~43	45	170~175	28.0	0.3	26.3	4.0	4.5	14.4	0.8	4.3
32	8.6	20	Ph_3P $NiBr_2$ CH_3J	1.0 0.4 0.3	56~34	54	170~175	18.2	0.4	28.8	1.2	5.3	4.2	0.8	5.2

a) The range of total pressure during the reaction period is shown.

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

c) The yield of crotonic acid (*trans*) was below 1%.

TABLE VI. CATALYTIC PROCESS USING METAL CARBONYLS

Hydroquinone, 0.1 g.

Run No.	C_3H_4 g.	CH_3OH ml.	Metal carbonyl g.	Additive ml.	CO[a)] Pressure atm.	CO[a)] Absorption amount %	Reaction temp. °C	Reaction time hr.	Recovered C_3H_4 g.	Product[b)] MMA %	Product[b)] MAA %	Product[b)] MC %	Product[b)] A %	Product[b)] HBM g.	Product[b)] Rd g.
25	6.3	20	$Ni(CO)_4$ 1.9	Concd. HCl 1.6	54~ 33(15)	34	160~170 190~200	2.0 9.7	0.1	31.7	1.4	3.2	15.5	1.0	1.7
23	7.7	20	2.0	1.7	77~ 30(26)	40	180~185	4.8	1.0	32.8	1.4	5.4	4.1	0.8	1.7
24	7.5	20	2.0	1.7	132~ 75(58)	48	198~202	11.5	0	33.2	1.9	5.9	18.4	0.3	1.3
22	8.4	20	$Ni(CO)_4$ 4.6	H_2O 0	88~ 82(29)	4	180~195	13.0	6.6	2.3	—	—	—	—	—
27	7.7	20	2.0	0	91~ 43(25)	33	200~205	6.0	Trace	12.0	0	3.1	Trace	0.3	7.5
28	7.4	20	2.0	0	150~128(59)	27	220~230	56	1.4	2.7	0	0.6	8.1	1.0	3.7
26	7.4	20	2.0	1.3	84~ 40(25)	54	200~205	6.6	Trace	37.8	1.3	8.1	1.9	0.8	3.1
31	11.7	18	2.0	2	82~ 36(25)	49	180~186	19.5	1.0	33.0	3.5	7.0	0.7	1.3	4.9
30	8.1	15	2.0	5	70~ 45(25)	56	165~170	15.7	0.2	32.0	13.5	6.6	0.9	1.0	2.4
67	8.0	50	$Co_2(CO)_8$ 0.5	H_2O 0	123~ 85(82)	44	150~155	7.5	2.5	Trace	0	—	Trace	0.9	5.1
65	9.6	20	1.8	5	140~116(30)	20	270~280	17.8	0	Trace	—	Trace	14.4	1.8	5.0
68	8.8	40	$Cr(CO)_6$ 0.6	H_2O 0	303~245(73)	16	280~293	16.0	0.4	Trace	0	Trace	3.2	1.1	5.6
66	8.8	20	1.5	5	141~137(29)	—	250~255	9.2	6.3	1.8	Trace	Trace	5.6	—	1.9
69	8.2	30	0.6	10	302~223(74)	41	280~290	13.3	0.2	5.5	—	2.0	6.0	2.1	7.4

a) See footnotes a) and b) in Table V. The values in parentheses show initial pressure (in first addition) of carbon monoxide at room temperature.

b) The maximum yields of methyl isobutyrate and crotonic acid were 1.0% (Run 24) and 1.7% (Run 30), respectively.

most of the methylacetylene was consumed in reacting with much smaller amounts of carbon monoxide. This implies that methylacetylene is liable to polymerize under the conditions, as might be supposed from the reports of Reppe and Schweckendiek,(16) and Meriwether et al.,(17) who have investigated the polymerization of acetylenes by triphenylphosphine nickel bromide and triphenylphosphine nickel carbonyl complexes. Thus, the yield of the carboxylation products would be improved by adopting a continuous method, because the addition of methylacetylene suppresses the polymerization of methylacetylene. Furthermore, a continuous addition of carbon monoxide at optimum partial pressure (about 10 atm.) would reduce the reaction time.

Acetone was formed in considerable yields (3∼24%) by the reaction of methylacetylene with water, which is formed by the formation of methyl ether from methanol. The ratio of methyl crotonate to methyl methacrylate was about 1 to 5; this ratio was much higher than that of the stoichiometric process where the reaction proceeded at lower temperatures (Table III). In all cases, methyl ether was formed in considerable quantities (10∼50%, based on the methanol used).

The nickel halides and triphenylphosphine nickel bromide complexes used as catalysts changed considerably in the reaction. In all cases nickel carbonyl was formed, probably by the following reaction: $NiBr_2+2CH_3OH+5CO \rightarrow Ni(CO)_4+2CH_3Br+H_2O+CO_2$. In Run 42 nickel carbonyl was obtained in a 20% yield (based on the nickel complex used). The nickel carbonyl formed may be supposed to participate in the carboxylation reaction, in view of the catalytic action of nickel carbonyl which will be mentioned below. In certain cases the formation of nickel hydroxide as fine precipitates was observed.

Metal Carbonyl Catalysts.—The results are shown in Table VI. In the case of the nickel carbonyl catalyst, all experiments, except Runs 22 and 31, were carried out in the presence of one-fourth of the theoretical amount of nickel carbonyl (based on methylacetylene). Runs 23–25 are examples of experiments which were carried out semi-catalytically. The total yield of methyl methacrylate and methacrylic acid was low (35%) under these conditions. The results, however, suggest the possibility that this process, especially in a continuous method, may be so developed as to become a good process for the synthesis of methyl methacrylate from methylacetylene, as in the case of the carboxylation of acetylene. Concerning the occurrence of the reaction, it was observed that the reaction required a high temperature when a high initial pressure of carbon monoxide was applied. The relation between the reaction temperature (lowest) and the pressure of carbon monoxide is shown in Fig. 2. However, in this figure the reaction temperature (80°C) in the case of the stoichiometric process was taken as that for zero atm. pressure of carbon monoxide.

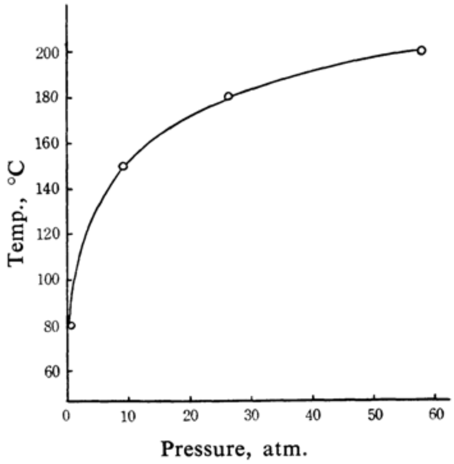


Fig. 2. Relation between the reaction temperature and the pressure (at room temp.) of carbon monoxide.

The reaction was similarly examined in the absence of hydrochloric acid. In cases where the acid was not added, scarcely any methyl methacrylate was formed at 180∼195°C (Run 22), and it was obtained in a low yield (12%) at 200∼205°C (Run 27). When water was present, the carboxylation reaction proceeded without the addition of any acid. This is an interesting fact, since it is generally known that nickel carbonyl without the addition of acid is not capable of forming acrylic esters from acetylene. The temperature at which the reaction occurred became lower as the amount of water was increased (Runs 26, 31, and 30). The reaction proceeded more readily in Run 30 (15 ml. methanol+5 ml. water) than in Run 23 (20 ml. methanol+1.7 ml. concentrated hydrochloric acid). The total yield of methyl methacrylate and methacrylic acid was better in the presence of water than in the presence of hydrochloric acid, and the best total yield was 46% (Run 30). Fortunately, by the use of water instead of hydrochloric acid, the formation of acetone (below 2%) and of methyl ether was suppressed.

In most cases, the greater part of the nickel

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16) W. Reppe and W. J. Schweckendiek, *Ann.*, **506**, 104 (1948).

17) L. S. Meriwether, E. C. Colthup, G. W. Kennerly and R. N. Reusch, *J. Org. Chem.*, **26**, 5155 (1961).

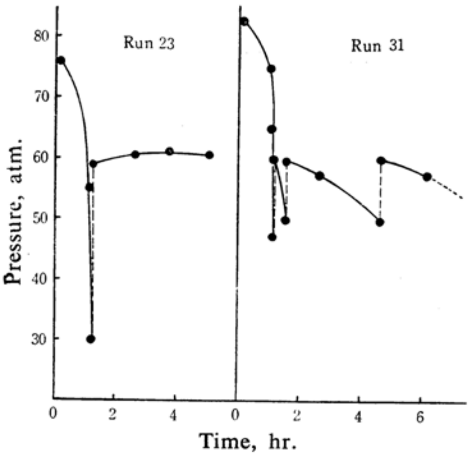

Fig. 3. Variation in total pressure with the reaction time-II.*
* The vertical broken lines show the added pressure of carbon monoxide.

carbonyl used as a catalyst was decomposed to give nickel chloride (in the presence of hydrochloric acid) or nickel hyroxide as fine precipitates. The decomposition was especially marked in cases where such a vigorous reaction as consumed, in a moment, all the carbon monoxide in the reaction vessel, occurred in the early stages of the reaction. Run 23 is given as an example of such cases in Fig. 3, which shows the variation in the total pressure of the reactants with the reaction time. In this run, the reaction stopped after the pressure fell rapidly, probably because of the decomposition of all the amounts of nickel carbonyl (compare with Run 31 in Fig. 3). Furthermore, it is noteworthy that such a vigorous reaction as has been described above appeared to result from two reactions of the carboxylation reaction and of the polymerization (inclusive of addition) reaction of methylacetylene, and that the latter reaction was probably a main cause of the poor yield of the carboxylation products. Thus, it may be supposed to be necessary, for keeping a long life of nickel carbonyl as a catalyst and for obtaining a better yield of methyl methacrylate, to add methylacetylene under controls. The performance of the carboxylation reaction by a semicontinuous method will be reported on in a subsequent publication.

Dicobalt octacarbonyl and chromium hexacarbonyl were not effective as catalysts for the carboxylation of methylacetylene (Runs 65—69). In the case of chromium hexacarbonyl, methyl methacrylate was obtained in only a slight yield (5%) in the presence of water and at the high temperature of 280～290°C (Run 69).

Summary

The synthesis of methyl methacrylate (MMA) by the carboxylation reaction of methylacetylene has been investigated.

Stoichiometric process: The carboxylation reaction was carried out under atmospheric pressure by premixing a 25～50 vol.% of acetylene in methylacetylene and under pressure (heating to 80°C). The total yields of MMA and MAA (methacrylic acid) were 45% (based on the methylacetylene consumed) under atmospheric pressure and 49% (66% (based on the nickel carbonyl used)) under pressure. Small amounts of methyl *trans*-crotonate, methyl isobutyrate, acetone, etc., were obtained as by-products, together with considerable amounts of high-boiling materials (not investigated).

Catalytic process: The reaction proceeded comparatively smoothly at 170～180°C and under about a 10 atm. partial pressure of carbon monoxide when triphenylphosphine nickel bromide complexes and nickel carbonyl-concentrated hydrochloric acid were used as catalysts. A triphenylphosphine nickel bromide catalyst, $(Ph_3P)_2NiBr_2$, gave the best total yield, 47%. It was found that, without the addition of acid, nickel carbonyl exhibits a catalytic action in the presence of water at 170～180°C. The total yield of MMA and MAA by this method was 46%. Fortunately, scarcely any acetone or methyl ether were formed. In view of this series of experimental results, it may be supposed that the poor total yield of MMA and MAA is chiefly due to the loss of methylacetylene by polymerization.

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Institute for Chemical Research
Kyoto University
Daigaku-cho, Takatsuki