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<th>Title</th>
<th>Synthesis of Methyl Methacrylate from Propylene</th>
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<tr>
<td>Author(s)</td>
<td>Kunichika, Sango; Sakakibara, Yasumasa</td>
</tr>
<tr>
<td>Citation</td>
<td>Bulletin of the Institute for Chemical Research, Kyoto University (1964), 42(4): 270-287</td>
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Kyoto University
The synthesis of methyl methacrylate from propylene through methylacetylene was investigated. The synthesis of methylacetylene was attempted by thermal dehydrogenation (pyrolysis) of propylene. High temperature (1200—1300°C), short contact time (millisecond order; conversions below 30%), and low pressure (below 100 mm.) were found to be required for obtaining good yields of methylacetylene-allene. The 32—38% yields of methylacetylene-allene on the basis of propylene pyrolyzed were obtained under best conditions. A free-radical mechanism was proposed for the pyrolysis to account for the experimental results. The synthesis of methyl methacrylate was performed by the carboxylation reaction of methylacetylene. The reaction was studied by both stoichiometric and catalytic processes. Stoichiometric process has been studied in the reaction carried out under pressure. The best total yield of methyl methacrylate and methacrylic acid was 49% based on the methylacetylene consumed (66% based on the nickel carbonyl used). As a catalytic process, the reaction proceeded fairly smoothly at 170—180°C and about 10 atm. partial pressure of carbon monoxide in the presence of triphenylphosphine nickel bromide complexes (47% total yield) or nickel carbonyl-water (46% total yield). The poor yields appeared chiefly to be due to the loss of methylacetylene by polymerization and addition reaction.

INTRODUCTION

Although methyl methacrylate has been manufactured commercially by the acetone cyanohydrin process, various new processes have been elaborately investigated. Recently, attentions have been drawn to two processes, one through the synthesis of methacrolein by air-oxidation of isobutylene (Methacrolein Process) and the other through the synthesis of α-hydroxy-isobutyric acid by nitric acid-oxidation of isobutylene (Escambia Process). But these processes have yet several points to be studied. The present authors noted the synthesis of methyl methacrylate by the carboxylation reaction of methylacetylene3 and took an interest in finding an economically valuable synthetic method of methylacetylene. Propylene was selected as the source material of methylacetylene, and the synthesis of methyl methacrylate by the following route was investigated:

\[
\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow{\text{Pyrolysis}} \text{CH}_3\text{C}=\text{CH} \xrightarrow{\text{Carboxylation}} \text{CH}_2=\text{CH} (\text{CH}_3) \text{CO}_2\text{CH}_3
\]

SYNTHESIS OF METHYLACETYLENE

The synthesis of methylacetylene from propylene was attempted by the pyrolysis. Although Rice, et al., have reported the synthesis of methylacetylene and allene3

---

*1 This is an outline of papers which are under contribution to Bull. Chem. Soc. Japan.
*2 国永三重, 橋原保正
*3 Methylacetylene and allene are isomeric and are equilibrated over catalysts at 250 to 300°C (See Ref. 5).
by the pyrolysis of isobutylene\textsuperscript{2}, none has been published concerning the synthesis of methylacetylene by the pyrolysis of propylene, except U. S. Pat.\textsuperscript{19} reported in course of this investigation. In the pyrolysis of propylene, though it was investigated by many workers, no one has detected methylacetylene in the products, while allene was found as a main product by Szwarc alone.\textsuperscript{49} He used extremely restricted conditions: temperature, 680—870°C; pressure, 2—15 mm.; conversion, 0.01—2%. The results obtained by Szwarc suggested that high temperature and low pressure may be required for the synthesis of methylacetylene-allene by the pyrolysis of propylene. The present authors investigated the pyrolysis under various conditions to find suitable conditions for the synthetic reaction.

**Experimental and Results**

The purity of propylene used was better than 99.0 mole %. A known amount (about one-fourth of the propylene volume) of cylinder nitrogen (99.9 mole % purity) was added to propylene as a reference gas to see the change of volume of the reactant gas in pyrolysis.

The apparatus and procedure are illustrated in Fig. 1. The reactant gas was introduced into a silica reaction tube (or porcelain in some cases) from the gas holder and pumped out by an oil pump through a 300 ml. glass gas sampling flask.

![Fig. 1. Apparatus for pyrolysis.](image)

Various silica tubes of 2.9 to 11.0 mm. inside diameter and two different types of electric furnaces, one 30 cm. long (furnace I) and the other 10 cm. long (furnace II), were employed for a series of experiments. The furnace II, constructed from a spiral "Siliconit" heating element, was used mainly for heating to 1100°C and above. The reaction tube was suspended in the center of another silica tube which extended through the furnace. The temperature was measured by a Pt-Pt•Rh thermocouple tied to the external wall of the reaction tube. The reactant gas feed and the pressure were regulated to the desired grades by means of the needle valve before the reaction tube and the microscrew clamp before the pump. The contact time was calculated by the formula:

$$\text{Contact time (sec.)} = \frac{V_R}{F},$$

(271)
where $V_R =$ volume of reaction zone (ml.) (20 cm. long with furnace I and 7 cm. long with furnace II).

$F =$ flow rate of reactant gas corrected to the temperature and the pressure of reaction zone (ml./sec.)

The analysis of the pyrolyzed gas was made by gas chromatography mainly using an 11.0 weight % $\beta,\beta'$-oxydipropionitrile-modified silica gel (60—80 mesh) column found by the present authors and a 30 weight % dioctyl phthalate column with hydrogen as a carrier gas. Gas chromatographic separations by these kinds of columns, of a mixture of air and hydrocarbons through $C_4$ are illustrated in Figs. 2 and 3. The absence of $C_3$-saturated hydrocarbons in the pyrolyzed gas made the analysis easy. Hydrogen was analyzed using the above liquid-modified silica gel column with nitrogen as a carrier gas.

![Chromatogram obtained using 2.5 m. column of silica gel modified with $\beta,\beta'$-oxydipropionitrile (8.0 weight %) at 70°C and flow rate 30 ml./min.](image)

*Fig. 2.* Chromatogram obtained using 2.5 m. column of silica gel modified with $\beta,\beta'$-oxydipropionitrile (8.0 weight %) at 70°C and flow rate 30 ml./min.

![Chromatogram obtained using 4.7 m. dioctyl phthalate (30 weight %) column at 28°C and flow rate 50 ml./min.](image)

*Fig. 3.* Chromatogram obtained using 4.7 m. dioctyl phthalate (30 weight %) column at 28°C and flow rate 50 ml./min.
Synthesis of Methyl Methacrylate from Propylene

The pyrolysis was performed under conditions varying over the following wide range: temperature, 800—1400°C; contact time, $4.4 \times 10^{-4} - 2.3$ sec.; pressure, 50—200 mm. (partial pressure of propylene, about 40—160 mm. Pressure shows the total pressure unless otherwise designated.) A part of the experimental results is shown in Table 1. Since methylacetylene and allene are equilibrated rapidly over catalysts, the total yield of them was shown to evaluate conditions for the synthesis of methylacetylene. In order to examine the hydrogen and carbon balance, the percentage of hydrogen and carbon in gaseous products ($H_2$ and $C_1$-$C_4$ hydrocarbons) was calculated from their yields.

**Effect of temperature on yield of methylacetylene-allene.** The yields of products obtained in the conversion range of 9 to 14% and at 100 mm. pressure are shown in Fig. 4 (also in Table 1). The yields of both methylacetylene ($M$-$C_3H_4$) and allene ($A$-$C_3H_4$) increased with increasing temperature in the range of 800 to 1400°C, and the total yield ($M+M$)-$C_3H_4$ ranged from 10 moles at 800°C up to 37 moles at 1300°C. Although the total yield increased rapidly in the lower part of the temperature range, it was almost constant (36 to 37 moles) at high temperature in the range of 1200 to 1400°C. Thus, a high temperature of 1200 to 1300°C was found to be suitable for the synthesis.

**Effect of contact time (conversion) on yield.** The results of the pyrolysis at 100 mm. and 1200°C are shown in Fig. 5. The yield of methylacetylene-allene decreased
### Table 1. Pyrolysis of propylene.

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<th>22</th>
<th>92*</th>
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<th>87</th>
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<td>1000</td>
<td>1100</td>
<td>1200</td>
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* Furnace I was used.

** Although propane was contained in small amount (less than 0.4%) as an impurity in the reactant gas, it was neglected, because its amount decreased with increasing conversion.

*** The total of butadiene and 2-butene was given as butadiene. The latter was found in much smaller amount than the former.
with increasing conversion, ranging from 36 moles at 10 % conversion down to 25 moles at 60 % conversion. Concerning each of them, the yield of allene fell at considerable rate as the conversion was increased, while that of methylacetylene was fairly constant at 13 to 15 moles over the wide conversion range. Such variations of the yields of methylacetylene and allene are explained on the basis of the fact that allene, a primary product of the pyrolysis, isomerizes to methylacetylene and the isomerization equilibrium is favored to methylacetylene.

**Effect of pressure on yield.** A number of experiments were carried out at 50, 100, and 200 mm. (partial pressure of propylene, about 40, 80, and 160 mm., respectively) and at 1200°C. The effect of pressure on the yield of methylacetylene and allene are shown in Fig. 6. Comparing the yields at fixed conversions, both the total and each yields increased with decreasing pressure. The differences in the total yields between different pressures were larger at higher conversion. The highest total yield of 40 moles was obtained when the pressure (50 mm.) and the conversion (9.0 %) were the lowest.

**Other products.** The other gaseous products were almost hydrogen, methane, and ethylene. In addition, smaller amounts of acetylene, 1-butene, butadiene, etc., were also obtained as gaseous products. The yields of these products did not vary with conditions of the pyrolysis, especially temperature, although the yields of methylacetylene and allene were affected seriously with temperature. The yields of methane
Table 2. Pyrolysis of allene*.
Composition of reactant gas, allene 74 % + propylene 6 % + nitrogen 20 %
Pressure, 100mm.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp., °C</th>
<th>Contact time, 10⁻³ sec.</th>
<th>Conversion, %</th>
<th>Volume ratio of methylacetylene/allene in pyrolyzed gas</th>
<th>Yield, moles/100 moles of allene pyrolyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>800</td>
<td>88</td>
<td>19.1</td>
<td>0.11</td>
<td>Hydrogen 2.6 7.5 3.0 7.7 2.7 7.3 10.9</td>
</tr>
<tr>
<td>8</td>
<td>1000</td>
<td>200</td>
<td>75.0</td>
<td>0.98</td>
<td>Methane 2.2 10.1 2.6 10.4 1.9 7.5 11.4</td>
</tr>
<tr>
<td>14</td>
<td>1200</td>
<td>4.4</td>
<td>28.4</td>
<td>0.29</td>
<td>Ethylene 7.2 7.1 3.3 4.5 3.3 2.6 3.4</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>16</td>
<td>80.2</td>
<td>1.91</td>
<td>Acetylene 1.0 4.1 1.5 7.5 1.0 7.0 11.9</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>0.40</td>
<td>14.5</td>
<td>1.47</td>
<td>Propylene** 3.2 0.2 1.9 (−2.0) 0.0 (−2.0) (−3.1)</td>
</tr>
<tr>
<td>19</td>
<td></td>
<td>0.81</td>
<td>68.0</td>
<td>1.94</td>
<td>Methylacetylene 47.1 32.9 72.4 47.3 86.6 69.0 53.8</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td>1.3</td>
<td>78.2</td>
<td></td>
<td>1-Butene (+Isobutene) 0.0 0.6 0.0 0.1 0.0 0.0 0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Butadiene (+2-Butenes) 0.0 0.4 0.0 0.6 0.0 0.5 1.0</td>
</tr>
</tbody>
</table>

Percentage of hydrogen and carbon in gaseous products (H₂, C₁–C₄ hydrocarbons)

<table>
<thead>
<tr>
<th>Hydrogen</th>
<th>Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.1</td>
<td>56.5</td>
</tr>
<tr>
<td>58.0</td>
<td>45.3</td>
</tr>
<tr>
<td>83.4</td>
<td>78.4</td>
</tr>
<tr>
<td>68.9</td>
<td>58.6</td>
</tr>
<tr>
<td>93.7</td>
<td>90.1</td>
</tr>
<tr>
<td>84.5</td>
<td>77.0</td>
</tr>
<tr>
<td>78.0</td>
<td>67.1</td>
</tr>
</tbody>
</table>

* Furnace I was used for Run 8 and furnace II for the others.
** The values were calculated in taking account of the amount of propylene contained in the reactant gas. The minus values shown in parentheses mean that propylene was pyrolyzed in the ratio of these values to 100 moles of allene pyrolyzed.
and ethylene, formed in a ratio of about 1 : 1, decreased with increasing temperature from about 50 moles to 40 moles and varied in a smaller degree with conversion and pressure (Table 1). The yields of hydrogen and acetylene increased with increasing temperature and conversion, and the maximum yields were 31 moles and 14 moles, respectively. 1-Butene and butadiene were obtained in smaller yields than 7 moles in many cases. Some amounts of higher hydrocarbons (C₅ and higher) and carbonaceous matter appeared to be formed because of the loss of the hydrogen and carbon in the gaseous products (Table 1).

**Discussion**

From Fig. 7, which shows the extrapolation of the gaseous products to zero conversion, it may be concluded that hydrogen, methane, ethylene, allene, and 1-butene are the primary products, and methylacetylene, acetylene, and butadiene are the secondary products. In addition, the results of the pyrolysis of allene itself, made as a reference investigation, showed that allene was much less stable than propylene and isomerized predominantly to methylacetylene at high temperature (1200°C) and low pressure (partial pressure of allene, 74 mm.) (Table 2).

The following free-radical mechanism is proposed for the pyrolysis to account for our experimental results.

**Primary Reactions**

\[
\begin{align*}
\text{CH}_2\text{=CH—CH}_3 & \rightarrow \text{CH}_2\text{=CH—CH}_2\cdot + \text{H} \\
\text{CH}_2\text{=CH—CH}_3 + \text{H} & \rightarrow \text{CH}_2\text{=CH—CH}_2\cdot + \text{H}_2 \\
\text{CH}_2\text{=CH—CH}_3 + \text{H} & \rightarrow \text{CH}_3—\text{CH}_2—\text{CH}_2\cdot \\
\text{CH}_3—\text{CH}_2—\text{CH}_2\cdot & \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3\cdot \\
\text{CH}_2\text{=CH—CH}_3 + \text{H}_2 & \rightarrow \text{CH}_2\text{=CH—CH}_2\cdot + \text{CH}_4 \\
\text{CH}_2\text{=CH—CH}_3 + \text{C}_2\text{H}_4 & \rightarrow \text{CH}_2\text{=CH—CH}_2\cdot + \text{higher hydrocarbons (HHC)(A)+H (CH}_2\cdot) \\
\text{CH}_2\text{=CH—CH}_3 + \text{C} & \rightarrow \text{CH}_2\text{=CH—CH}_3 + \text{H} \\
\text{CH}_2\text{=CH—CH}_3 + \text{H} & \rightarrow \text{CH}_2\text{=CH—CH}_3 + \text{CH}_3\cdot \\
\text{CH}_2\text{=CH—CH}_3 + \text{CH}_3\cdot & \rightarrow \text{CH}_2\text{=CH—CH}_3 + \text{CH}_4 \\
\text{CH}_2\text{=CH—CH}_3 + \text{CH}_2\text{=CH—CH}_2\cdot & \rightarrow \text{HHC}(B)+\text{H} \\
\text{CH}_2\text{=CH—CH}_3 + \text{CH}_2\text{=CH—CH}_2\cdot & \rightarrow \text{HHC}(C)+\text{H} \\
\text{CH}_2\text{=CH—CH}_3 + \text{CH}_2\text{=CH—CH}_2\cdot & \rightarrow \text{HHC}(D)+\text{H} \\
\text{CH}_2\text{=CH—CH}_3 + \text{C}_2\text{H}_4 & \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2\cdot \\
\text{CH}_2\text{=CH—CH}_3 + \text{C}_2\text{H}_4 & \rightarrow \text{CH}_2\text{=CH—CH}_3 + \text{C}_2\text{H}_5 \\
\text{CH}_2\text{=CH—CH}_3 + \text{CH}_2\text{=CH—CH}_2\cdot & \rightarrow \text{HHC}(E)+\text{H} \\
\text{CH}_2\text{=CH—CH}_3 + \text{CH}_2\text{=CH—CH}_2\cdot & \rightarrow \text{HHC}(F)+\text{H} \\
\text{CH}_2\text{=CH—CH}_3 + \text{C}_2\text{H}_4 & \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2\cdot \\
\text{CH}_2\text{=CH—CH}_3 + \text{C}_2\text{H}_4 & \rightarrow \text{CH}_2\text{=CH—CH}_3 + \text{C}_2\text{H}_5 \\
\text{CH}_2\text{=CH—CH}_3 + \text{CH}_2\text{=CH—CH}_2\cdot & \rightarrow \text{HHC}(G)+\text{H} \\
\text{CH}_2\text{=CH—CH}_3 + \text{CH}_2\text{=CH—CH}_2\cdot & \rightarrow \text{HHC}(H)+\text{H} \\
\text{CH}_2\text{=CH—CH}_3 + \text{C}_2\text{H}_4 & \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2\cdot \\
\text{CH}_2\text{=CH—CH}_3 + \text{C}_2\text{H}_4 & \rightarrow \text{CH}_2\text{=CH—CH}_3 + \text{C}_2\text{H}_5 \\
\text{CH}_2\text{=CH—CH}_3 + \text{CH}_2\text{=CH—CH}_2\cdot & \rightarrow \text{HHC}(I)+\text{H} \\
\end{align*}
\]

In this mechanism, special attention has been given to the formation of allene and methylacetylene and to their subsequent decomposition, and the following restrictions are imposed. Secondary reactions involving stable products such as methane and ethylene are neglected. Although higher hydrocarbons (C₅ and higher) formed in the pyrolysis would readily undergo subsequent decomposition, these reactions are also neglected.
In this mechanism, the primary reactions (reactions 1—9) proceed in a chain process. Namely, reaction 1 is the chain initiation, reactions 2—6, 2—7, 3—4—5—6, and 3—4—5—7 are the chain propagations, and reactions 8 and 9 are the chain terminations. Reaction 6 has been proposed for the formation of higher hydrocarbons by Laidler and Wojciechowski who obtained benzene, cyclopentadiene, etc., as the liquid products in the pyrolysis.

As far as secondary reactions are concerned, those involving allene and its isomerization product, methylacetylene, may be presumed to be predominant on the basis of relative stability of propylene and allene (Table 3). Allene isomerizes to methylacetylene (reaction 10), and the methylacetylene/allene ratio approaches to the value of the equilibrium constant for the isomerization (Table 4). It has been shown by Collin and Lossing that the loss of an H atom from allene results in the formation of a C5H3 radical which has a propargyl configuration rather than an allenyl one and that the forms CH==C—CH2 and CH==C—CH2 are probably resonance hybrids. Reactions 11, 12, and 13 represent the formation of higher hydrocarbons from allene, methylacetylene, and their radicals.

Table 3. Relative stability of propylene and allene.

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion, %</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Contact time*, sec.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene</td>
<td>2.1</td>
<td>1.3 x 10^-2</td>
<td>1.9 x 10^-3</td>
</tr>
<tr>
<td>Allene**</td>
<td>8.9 x 10^-2</td>
<td>3.7 x 10^-3</td>
<td>4.4 x 10^-4</td>
</tr>
<tr>
<td>(0.10)</td>
<td>(8.2 x 10^-3)</td>
<td>(8.1 x 10^-4)</td>
<td>(1.5 x 10^-3)</td>
</tr>
<tr>
<td>Ratio of contact time, propylene/allene</td>
<td>24</td>
<td>3.5</td>
<td>4.3</td>
</tr>
<tr>
<td>(21)</td>
<td>(1.6)</td>
<td>(2.4)</td>
<td>(2.0)</td>
</tr>
</tbody>
</table>

* Contact times for fixed conversions were obtained from curves of contact time vs. conversion.
** The values shown in parentheses are those of cases in which conversion was calculated regarding both allene and its isomerization product, methylacetylene, as unreacted allene.

Table 4. Equilibrium constant for isomerization of allene*.

<table>
<thead>
<tr>
<th>Temp., °K</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
<th>1400</th>
<th>1500</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_p = [CH==C—CH2] / [CH==C—CH2]</td>
<td>4.53</td>
<td>3.75</td>
<td>3.15</td>
<td>2.94</td>
<td>2.77</td>
</tr>
</tbody>
</table>

* The values were calculated based on ΔG°/T given in “Landolt-Börnstein Zahlenwerte und Funktionen,” 6 Aufl. II. Bd. 4. Teil, 543 (1961); See also J. F. Cordes and H. Günzler, Chem. Ber., 92, 1055 (1959).

The compatibility of the proposed mechanism with the experimental data can now be examined. According to this mechanism, the ethylene/methane ratio is required to be about 1 : 1. The experimental data seem to confirm this (Table 1). The hydrogen/ethylene ratio should be independent of the pressure of propylene since reactions 2 and 3 are the same reactions of propylene with hydrogen atom. This was well consistent
Synthesis of Methyl Methacrylate from Propylene

with the experimental data (Table 1). Furthermore, the activation energies for both reactions are small (both 1.5 Kcal./mole), and therefore, the hydrogen/ethylene ratio should be nearly independent of temperature. The experimental data seem to confirm this requirement considering that the pyrolysis was made over a wide range of temperature.

Now, inspections are made of allene and methylacetylene. According to this mechanism, one allyl radical is produced per each mole of hydrogen (reaction 2) or methane (reaction 5). In addition, allyl radicals are produced by the chain initiation reaction 1. These allyl radicals disappear in any one of four reactions 6, 7, 8, and 9. Apart from reactions 8 and 9, which are the chain-terminating reactions, the rates of formation of higher hydrocarbons by reaction 6 ($v_6$) and allene by reaction 7 ($v_7$) are compared. Table 5 shows the $v_6/v_7$ ratio at various temperature and 80 mm. pressure of propylene. The ratio was calculated based on kinetic parameters assumed by Laidler and Wojciechowski:

$$v_6 = \frac{k_6}{k_7} \times \frac{[C_2H_4]}{[C_2H_5]} = 10^{-7.8} \times e^{55000/RT} \times 1.28/T$$

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_6/v_7$</td>
<td>5.0</td>
<td>0.40</td>
<td>0.062</td>
<td>0.013</td>
</tr>
</tbody>
</table>

and Wojciechowski: $E_6$ (activation energy) = 15 Kcal./mole and $A_6$ (frequency factor) = $10^6$ 1./mole-sec. for reaction 6, and $E_7$ = 70 Kcal./mole and $A_7 = 10^{12.0}$ sec.$^{-1}$ for reaction 7. From the calculated values it follows that at 900°C the rate of reaction 7 is more rapid than that of reaction 6 and reaction 6 is practically neglected above 1000°C. Thus, the results of the theoretical calculation show that temperature has a remarkable effect on the yield of allene-methylacetylene and that high temperature is suitable for the formation of allene-methylacetylene. As another cause for requiring high temperature (100—1300°C), it may be concluded that at high temperature allene isomerizes to methylacetylene predominantly (Table 2), and allene and methylacetylene are comparatively stable (Table 3).

The rapid decrease of the yield of allene-methylacetylene with the increase of conversion may be supposed to be due to the loss of allene, methylacetylene, and propylene, probably by various secondary reactions involving reactions 10 to 14. The variation of the methylacetylene/allene ratio with conversion can be accounted for by the equilibrium relation between them. Namely, the experimental ratio (1.6 at 56 % conversion) approached to the calculated equilibrium constant (3.0 at 1100°C) with increasing conversion (Fig. 7).

The decrease of pressure of propylene suppresses secondary reactions 11 to 14 by which allene, methylacetylene, and propylene are lost, in addition to reaction 6 leading to the formation of higher hydrocarbons. This explains that low pressure is suitable for the formation of allene-methylacetylene.

**SYNTHESIS OF METHYL METHACRYLATE**

The synthesis of methyl methacrylate from methylacetylene was performed by
Numerous investigations have been made on the synthesis of acrylic esters by the carboxylation of acetylene, and the following three processes are known:

(1) Stoichiometric Process
\[ 4\text{CH}_2=\text{C}+\text{Ni(CO)}_4+4\text{ROH}+2\text{HCl} \rightarrow 4\text{CH}_2=\text{CHCO}_2\text{R}+\text{NiCl}_2+\text{H}_2 \]

(2) Catalytic Process
\[ \text{Catalyst} \quad \text{CH}_2=\text{C}+\text{CO}+\text{ROH} \rightarrow \text{CH}_2=\text{CHCO}_2\text{R} \]
Catalyst: Nickel halides, Triphenylphosphine nickel complexes, etc.

(3) Semicatalytic Process
\[ \text{Stoichiometric process plus} \quad \text{Ni(CO)}_4 \rightarrow \text{CH}_2=\text{CHCO}_2\text{R} \]

Concerning the carboxylation of methylacetylene, however, very little has been published. One literature by Yakubovich and Volkova and one patent have described the synthesis of methacrylic acid and its lower alkyl esters by the stoichiometric process (low yields). Most recently, it has been reported by another patent that aminoalkyl methacrylates were synthesized in fairly good yields from methylacetylene by the semicatalytic process. Jones, et al., investigating the carboxylation of various monosubstituted acetylenes by the stoichiometric process, obtained ethyl α-butylacrylate in 50% yield from butylacetylene. In the present investigation, the carboxylation reaction was examined by both stoichiometric and catalytic (inclusive of semicatalytic) processes and in a batch manner, except for cases where the reaction was carried out under atmospheric pressure.

**Stoichiometric Process**

**Carboxylation under atmospheric pressure.** The carboxylation reaction was performed by introducing methylacetylene (purity, above 98.5 mole %) or a mixed gas with acetylene into a solution of methanol and concd. hydrochloric acid with dropping nickel carbonyl under vigorous stirring. Whenever the reaction began, a transient brown coloration and a rise in temperature were observed. After dropping all amounts of nickel carbonyl, the reactant gas was introduced until the absorption stopped practically. During the reaction period, sometimes a portion of the gas in the flask was sent into a waste gas holder. The analysis of products was made mainly by gas chromatography. General procedures for the analysis and the gas chromatographic columns used are summarized in Fig. 8. The results of the carboxylation are shown in Table 6. By this method methylacetylene was not carboxylated so rapidly as acetylene. Even at 73–76°C, no obvious reaction occurred, and methyl methacrylate (MMA) was obtained in a poor yield (3.6%). (The yield was based on the methylacetylene consumed unless otherwise designated.) Although the greater part (70%) of nickel carbonyl was decomposed, most of carbon monoxide resulting from the decomposition was present.

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84 This process is a modification of the Reppe stoichiometric process, namely, a catalytic reaction of carbon monoxide, acetylene, and alcohol is superimposed upon the stoichiometric process. In this paper, this process is treated as a catalytic process.
Synthesis of Methyl Methacrylate from Propylene

Gas chromatography

<table>
<thead>
<tr>
<th>Analyzed compound</th>
<th>Column</th>
<th>Temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂, H₂, CH₄, CO</td>
<td>Molecular Sieve 6A (2.4 m.)</td>
<td>60</td>
</tr>
<tr>
<td>Hydrocarbons, Other gaseous products</td>
<td>SA (2.4 m.)</td>
<td>RT</td>
</tr>
<tr>
<td>30 % Diocyl phthalate (4.7 m.)</td>
<td>RT</td>
<td></td>
</tr>
<tr>
<td>8.0 % β,β'-Oxydipropionitrile on silica gel (2.5 m.)</td>
<td>70</td>
<td></td>
</tr>
</tbody>
</table>

Waste gas ......................................................30 % Dioctyl ReP Hydrocarbons, phthalate (4.7 m.)

Reaction mixture
dil. H₃SO₄, Extracted (CH₂Cl₂)

Methylene chloride extract

A or B Distilled

Low boiling fraction (−80°C/150 mm.)

High boiling fraction (60-100°C/50 mm.)

Esters, Acetone

Carboxylic acids

Acidic Acidified, Extracted (CH₂Cl₂) Distilled

Neutral fraction Distilled

Distillate

Carboxylic acids

Distillate

Fig. 8. Scheme for analysis.

a), b), and c) p-Xylene, toluene, and chlorobenzene were used internal standard substances, respectively.

d) By the fractionation the following compounds were isolated and identified: Acetone; b.p. 56-7°C: 2,4-dinitrophenyl hydrazone; m.p. 125°C (Found: N, 23.62).
Methyl methacrylate; b.p. 47-8°C/112 mm., nD₂₀ 1.4149, d₄₂° 0.947 (Found: C, 60.04; H, 8.25).
Methyl crotonate (trans); b.p. 57-8°C/84 mm., nD₂₀ 1.4248, d₄₂° 0.944 (Found: C, 59.85; H, 8.36).

in the waste gas as free carbon monoxide. We found that the addition of acetylene accelerated the reaction considerably. When a mixed gas of methylacetylene and acetylene in 1 : 1 to 2 : 1 ratio was employed, a vigorous exothermic reaction occurred after a short induction period, though, in the case of the 3 : 1, the reaction proceeded fairly slowly (Runs 56—58). In the case of the 2 : 1 ratio the total yield of MMA and MAA (methacrylic acid) was 45 %, the best yield of Runs 56—58, while the total yield of methyl acrylate and acrylic acid produced from acetylene was 66 %. In view of these experimental results, it is likely that, compared with acetylene, methylacetylene is difficult to carboxylate, but polymerize easily and/or add to olefinic compounds such as MMA, methyl acrylate, etc., under conditions of the carboxylation reaction.

Methyl crotonate (trans), methyl isobutyrate, and acetone were obtained as by-products from methylacetylene. The processes of formation of these substances are as follows:

\[
\begin{align*}
(CH_3)_2CHCO_2CH_3 & \quad \overset{H_2 \text{ (active Ni from Ni(CO)₄)}}{\longrightarrow} \\
CH_2=CH(CO)OH & \quad \overset{Ni(CO)₄}{\longrightarrow} \\
CH=CHCH₃ & \quad \overset{H^+, H_2O}{\longrightarrow} \\
(CH_3)CHCO_2CH_3 & \quad \overset{H^+, H_2O}{\longrightarrow} \\
\end{align*}
\]

(281)
### Table 6. Stoichiometric process under atmospheric pressure.

Methanol, 32 ml.; Conc. hydrochloric acid, 20 ml.; Hydroquinone, 0.1 g.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acetylenes and nickel carbonyl</th>
<th>Reaction temp. °C</th>
<th>Reaction time hr.-min.</th>
<th>Recovered acetylenes C₃H₄ l, C₂H₂ l</th>
<th>Productsa) From C₃H₄</th>
<th>Products From C₂H₂</th>
<th>HBM g</th>
<th>Rd g</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>C₃H₄ 3.55 l. Ni (CO)₄ 4.8 g.</td>
<td>73-76</td>
<td>4.00</td>
<td>1.61 (2.7 g.) 0.24</td>
<td>3.6 (2.7) Trace</td>
<td>MC Trace</td>
<td>6.0</td>
<td>0.8</td>
</tr>
<tr>
<td>58</td>
<td>C₃H₄–C₂H₂ 1:1 Ni (CO)₄ 17.0 g.</td>
<td>38-48</td>
<td>2.08</td>
<td>0.20 (0.6 g.) 0.55</td>
<td>35.6 (43.6) 3.8</td>
<td>MIB 1.2</td>
<td>A 2.1</td>
<td>3.7</td>
</tr>
<tr>
<td>56</td>
<td>C₃H₄–C₂H₂ 2:1 Ni (CO)₄ 17.6 g.</td>
<td>50-57</td>
<td>3.50</td>
<td>0.99 (1.1 g.) 0.55</td>
<td>40.7 (43.2) 4.0</td>
<td>MC 0.3</td>
<td>A 2.1</td>
<td>5.6</td>
</tr>
<tr>
<td>57</td>
<td>C₃H₄–C₂H₂ 3:1 Ni (CO)₄ 17.1 g.</td>
<td>54-58</td>
<td>4.30</td>
<td>0.35 (0.6 g.) 0.12</td>
<td>30.0 (37.2) 1.9</td>
<td>MIB 0.8</td>
<td>A 1.9</td>
<td>7.9</td>
</tr>
<tr>
<td>59b)</td>
<td>C₃H₄ 4.57 l. Ni (CO)₄ 7.7 g.</td>
<td>72-76</td>
<td>3.00</td>
<td>0.2 (2.7 g.)</td>
<td>BMA 16.1 (17.1) 1.2</td>
<td>A 4.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 concd. hydrochloric acid (10 ml.) were used. BMA=Butyl methacrylate.

### Table 7. Stoichiometric process under pressure.

Methanol, 30 ml.; Conc. hydrochloric acid, 12 ml.; Nickel carbonyl, 10.7 g.; Hydroquinone, 0.1 g.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>C₃H₄ g.</th>
<th>C₃H₄/Ni (CO)₄ Equivalent ratio</th>
<th>Reaction temp. °C</th>
<th>Reaction time min.</th>
<th>Recovered C₃H₄ g.</th>
<th>Productsa)</th>
<th>HBM g</th>
<th>Rd g</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>10.4</td>
<td>1.03</td>
<td>16-80</td>
<td>55</td>
<td>Trace</td>
<td>36.8 (38.0)</td>
<td>4.9</td>
<td>0.8</td>
</tr>
<tr>
<td>63</td>
<td>13.5</td>
<td>1.34 (1.23)b)</td>
<td>80-116</td>
<td>40</td>
<td>1.1</td>
<td>44.5 (5.50)</td>
<td>4.9</td>
<td>2.3</td>
</tr>
<tr>
<td>15</td>
<td>14.7</td>
<td>1.46</td>
<td>90-120</td>
<td>90</td>
<td>—</td>
<td>(58.8)</td>
<td>(7.4)</td>
<td>1.7</td>
</tr>
</tbody>
</table>

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 the methylacetylene absorbed to the theoretical value based on the nickel carbonyl used.
Synthesis of Methyl Methacrylate from Propylene

**Carboxylation under pressure.** Into a 100 ml. autoclave provided with electromagnetic stirrer were charged methanol, concd. hydrochloric acid, nickel carbonyl, and hydroquinone under nitrogen. The vessel was cooled and evacuated, and methylacetylene was added by distillation. The vessel was heated slowly to the reaction temperature. The results are shown in Table 7. In all cases, a vigorous exothermic reaction occurred at about 80°C, as observed by a sudden marked rise in temperature, for example, from 80 to 105°C in Run 16. In Run 63 where a excess of methylacetylene was used, a quantity of 1.23 times of the theoretical amount of methylacetylene (based on the nickel carbonyl used) was absorbed, and MMA was obtained in 45%, yield together with MAA in 5% yield. On the other hand, the best total yield of MMA and MAA based on the nickel carbonyl used was 66% (Run 15). Considerable amounts of higher boiling materials (b.p. 87—92°C/47 mm. in Run 15), were formed. They appeared to be C₇ olefinic esters formed by the dimerization of methylacetylene and subsequent carboxylation and/or by the addition of methylacetylene to MMA, though no further study was made.

Notwithstanding that hydrogen is formed according to the reaction formula, only 16% of the theoretical amount of hydrogen, in Run 63, was found in the waste gas (gas remained in autoclave, 1920 ml.) as free (4 ml.) or combined hydrogen (propylene 227 ml.). Furthermore, in view of the fact that the yield of methyl isobutyrate also was small, it may be concluded that most of hydrogen must add to the higher boiling materials and residue.

**Catalytic Process**

Into a 100 ml. autoclave provided with electromagnetic stirrer was charged the reactants in the same manner as described above. Carbon monoxide was added to a pressure of 15 to 25 atm. in most cases. During the period of reaction, whenever the partial pressure of carbon monoxide fell down to about 10 atm. (At 170°C, about 30 atm. pressure resulted from a mixture of methanol (20 ml.) and methylacetylene (8 g.)) carbon monoxide was pressed in repeatedly to maintain a partial pressure of 10 to 40 atm. In most cases, the reaction was continued until the absorption of carbon monoxide ceased practically.

**Nickel halide and triphenylphosphine nickel bromide complex catalyst.** The results are shown in Table 8. Generally, in the presence of these catalysts the reaction proceeded fairly smoothly at a temperature of 170—180°C and about 10 atm. partial pressure of carbon monoxide, as illustrated by the variation of total pressure in Fig. 9. Triphenylphosphine nickel bromide and triphenylphosphine nickel bromide-butyl bromide complexes gave better results than those of nickel bromide and iodide, though these complexes have been reported to decompose with the separation of triphenylphosphine in methanol. The total yield, of MMA and MAA was unsatisfactory (best yield, 47% in Run 44). This poor yield appeared chiefly to be due to the loss of methylacetylene by the formation of high molecular substances (expressed as HBM and Rd in Table 8). Particularly, large amounts of high molecular substances were formed in cases where a vigorous exothermic reaction occurred in the
early stage of the reaction, as shown by a marked fall in pressure (Run 41 in Table 8 and Fig. 9). Such a vigorous reaction appeared to be resulted from the polymerization (inclusive of addition) reaction\(^{*5}\) of methylacetylene in addition to the carboxylation reaction, because most of methylacetylene was consumed at that time in spite of a marked insufficiency of carbon monoxide. If so, the yield of the carboxylation products would be improved by adopting a continuous method, since the addition of methylacetylene in little portions suppresses the polymerization of methylacetylene. Furthermore, a continuous addition of carbon monoxide at optimum partial pressure (about 10 atm.) would shorten the reaction time.

Acetone was formed in considerable yields (3—24 \%) by the addition reaction to methylacetylene of water resulted from reaction: methanol\(\rightarrow\)methyl ether + water. The ratio of methyl crotonate to MMA increased fairly, compared with the stoichiometric process where the reaction was carried out at lower temperature.

The catalysts appeared to change in quality markedly. In any case, some amounts of nickel carbonyl were formed, probably by the following equation: \(\text{NiBr}_2 + 2\text{CH}_2\text{OH} + 5\text{CO} \rightarrow \text{Ni(CO)}_4 + 2\text{CH}_3\text{Br} + \text{H}_2\text{O} + \text{CO}_2\). In certain cases the formation of nickel hydroxide as fine precipitates was observed.

**Nickel carbonyl catalyst.** The results are shown in Table 9. 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 the examples of experiments which were made by the semicatalytic process. The total yield of MMA and MAA was low (35 \%) under these conditions. The results, however, suggest the possibility that this process, especially in a continuous method, may be adopted as a

\(^{*5}\) Reppe and Schweckendiek (Ann., 560, 104 (1948)), and Meriwether, et al. (J. Org. Chem., 26, 5155, 5163 (1961)), have reported the polymerization of acetylenes by triphenylphosphine nickel bromide and triphenylphosphine nickel carbonyl complexes.
Table 8. Catalytic process using nickel halides and triphenylphosphine nickel bromide complexes.
Hydroquinone, 0.05 g.

<table>
<thead>
<tr>
<th>Run</th>
<th>C₂H₄</th>
<th>CH₃OH</th>
<th>Catalyst</th>
<th>CO Pressure</th>
<th>Absorption amount</th>
<th>Reaction temp.</th>
<th>Reaction time</th>
<th>Recovered C₃H₄</th>
<th>MMA</th>
<th>MAA</th>
<th>MC</th>
<th>A</th>
<th>HBM</th>
<th>Rd</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>g.</td>
<td>ml.</td>
<td>g.</td>
<td>atm.</td>
<td>%</td>
<td>°C</td>
<td>hr.</td>
<td>g.</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>g.</td>
<td>g.</td>
</tr>
<tr>
<td>20</td>
<td>8.2</td>
<td>20</td>
<td>NiBr₂</td>
<td>1.5</td>
<td>64-39</td>
<td>170-175</td>
<td>16.0</td>
<td>0.7</td>
<td>18.0</td>
<td>0.7</td>
<td>2.3</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>6.3</td>
<td>15</td>
<td>Ni Br₂</td>
<td>1.5</td>
<td>75-38</td>
<td>168-173</td>
<td>36</td>
<td>0</td>
<td>29.3</td>
<td>—</td>
<td>5.1</td>
<td>1.5</td>
<td>4.8</td>
<td>1.5</td>
</tr>
<tr>
<td>18</td>
<td>5.0</td>
<td>15</td>
<td>CH₃ J</td>
<td>0.13</td>
<td>(unreacted)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>8.4</td>
<td>20</td>
<td>(Ph₃ P)₂ Ni Br₂</td>
<td>1.4</td>
<td>57-31</td>
<td>168-174</td>
<td>9.8</td>
<td>24.8</td>
<td>2.8</td>
<td>4.8</td>
<td>1.5</td>
<td>2.8</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>7.6</td>
<td>„</td>
<td>„</td>
<td>„</td>
<td>63-36</td>
<td>170-175</td>
<td>19.6</td>
<td>0.2</td>
<td>18.0</td>
<td>1.1</td>
<td>3.4</td>
<td>2.6</td>
<td>0.8</td>
<td>6.5</td>
</tr>
<tr>
<td>44</td>
<td>8.0</td>
<td>„</td>
<td>„</td>
<td>„</td>
<td>71-40</td>
<td>„</td>
<td>21.5</td>
<td>0.3</td>
<td>38.9</td>
<td>1.9</td>
<td>7.2</td>
<td>2.8</td>
<td>1.1</td>
<td>3.6</td>
</tr>
<tr>
<td>42</td>
<td>7.1</td>
<td>„</td>
<td>(Ph₃ P)₂ Ni Br₂</td>
<td>1.7</td>
<td>57-38</td>
<td>„</td>
<td>19.7</td>
<td>0.1</td>
<td>36.0</td>
<td>2.0</td>
<td>6.5</td>
<td>6.9</td>
<td>0.7</td>
<td>4.5</td>
</tr>
</tbody>
</table>

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 lower than 1%.

Table 9. Catalytic process using nickel carbonyl.
Hydroquinone, 0.1 g.

<table>
<thead>
<tr>
<th>Run</th>
<th>C₂H₄</th>
<th>CH₃OH</th>
<th>Metal carbonyl</th>
<th>Additive</th>
<th>CO Pressure</th>
<th>Absorption amount</th>
<th>Reaction temp.</th>
<th>Reaction time</th>
<th>Recovered C₃H₄</th>
<th>MMA</th>
<th>MAA</th>
<th>MC</th>
<th>A</th>
<th>HBM</th>
<th>Rd</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>g.</td>
<td>ml.</td>
<td>g.</td>
<td>ml.</td>
<td>atm.</td>
<td>%</td>
<td>°C</td>
<td>hr.</td>
<td>g.</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>g.</td>
<td>g.</td>
</tr>
<tr>
<td>25</td>
<td>6.3</td>
<td>20</td>
<td>Ni(CO)₄</td>
<td>Conc. HCl</td>
<td>54-33 (15)</td>
<td>34</td>
<td>160-170</td>
<td>2.0</td>
<td>0.1</td>
<td>31.7</td>
<td>1.4</td>
<td>3.2</td>
<td>15.5</td>
<td>1.0</td>
<td>1.7</td>
</tr>
<tr>
<td>23</td>
<td>7.7</td>
<td>„</td>
<td>„</td>
<td>„</td>
<td>77-30 (26)</td>
<td>40</td>
<td>180-185</td>
<td>4.8</td>
<td>1.0</td>
<td>32.8</td>
<td>1.4</td>
<td>5.4</td>
<td>4.1</td>
<td>0.8</td>
<td>1.7</td>
</tr>
<tr>
<td>24</td>
<td>7.5</td>
<td>„</td>
<td>„</td>
<td>„</td>
<td>132-75 (58)</td>
<td>48</td>
<td>198-202</td>
<td>11.5</td>
<td>0</td>
<td>33.2</td>
<td>1.9</td>
<td>5.9</td>
<td>18.4</td>
<td>0.3</td>
<td>1.3</td>
</tr>
<tr>
<td>22</td>
<td>8.4</td>
<td>„</td>
<td>Ni(CO)₄</td>
<td>H₂O</td>
<td>88-82 (29)</td>
<td>4</td>
<td>180-195</td>
<td>13.0</td>
<td>6.6</td>
<td>2.3</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>27</td>
<td>7.7</td>
<td>„</td>
<td>„</td>
<td>„</td>
<td>91-43 (25)</td>
<td>33</td>
<td>200-205</td>
<td>6.0</td>
<td>Trace</td>
<td>12.0</td>
<td>0</td>
<td>3.1</td>
<td>Trace</td>
<td>0.3</td>
<td>7.5</td>
</tr>
<tr>
<td>28</td>
<td>7.4</td>
<td>„</td>
<td>„</td>
<td>„</td>
<td>150-128 (59)</td>
<td>27</td>
<td>220-230</td>
<td>56</td>
<td>1.4</td>
<td>2.7</td>
<td>0</td>
<td>0.6</td>
<td>8.1</td>
<td>1.0</td>
<td>3.7</td>
</tr>
<tr>
<td>26</td>
<td>7.4</td>
<td>„</td>
<td>„</td>
<td>„</td>
<td>84-40 (25)</td>
<td>54</td>
<td>200-205</td>
<td>6.6</td>
<td>Trace</td>
<td>37.8</td>
<td>1.3</td>
<td>8.1</td>
<td>1.9</td>
<td>0.8</td>
<td>3.1</td>
</tr>
<tr>
<td>31</td>
<td>11.7</td>
<td>18</td>
<td>„</td>
<td>„</td>
<td>82-36 (25)</td>
<td>49</td>
<td>180-186</td>
<td>19.5</td>
<td>1.0</td>
<td>33.0</td>
<td>3.5</td>
<td>7.0</td>
<td>0.7</td>
<td>1.3</td>
<td>4.9</td>
</tr>
<tr>
<td>30</td>
<td>8.1</td>
<td>15</td>
<td>„</td>
<td>„</td>
<td>70-45 (25)</td>
<td>56</td>
<td>165-170</td>
<td>15.7</td>
<td>0.2</td>
<td>32.0</td>
<td>13.5</td>
<td>6.6</td>
<td>0.9</td>
<td>1.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>

a) See footnote a) and b) in Table 8. 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.
good process for the synthesis of MMA from methylacetylene, as the case of acetylene. Concerning the pressure of carbon monoxide, it was observed that the reaction occurred at lower temperature and proceeded at faster rate as the initial pressure was lowered. The relation between the reaction temperature and the pressure of carbon monoxide is shown in Fig. 10, on the assumption that the reaction temperature (80°C) at the stoichiometric process corresponds to that of zero atm. pressure of carbon monoxide.

![Fig. 10. Relation between reaction temperature and pressure (at room temp.) of carbon monoxide.](image)

In connection with the above process, in the absence of hydrochloric acid the reaction was examined similarly. In the cases where the acid was not present, MMA was hardly formed at 180—185°C (Run 22) and obtained in low yield (12%) at 200—205°C (Run 27). When water was present, the carboxylation reaction proceeded without any acids. This is an interesting fact, since in general it is known that nickel carbonyl does not react to form acrylic esters without addition of acid. The reaction temperature was lowered 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. concd. hydrochloric acid). The best total yield of MMA and MAA was 46 % (Run 30) and was better than that in the presence of hydrochloric acid. Advantageously, in the absence of hydrochloric acid, the formation of acetone (below 2 %) and methyl ether was suppressed.

In the case of nickel carbonyl catalyst the carboxylation reaction appeared to be accompanied with the polymerization (inclusive of addition reaction) of methylacetylene. Namely, in the early stage of the reaction, a vigorous exothermic reaction occurred under a marked insufficiency of carbon monoxide to consume the greater part of methylacetylene, and most of nickel carbonyl was decomposed (Run 31). Accordingly, a better yield of MMA would be given by adopting a continuous method.
Synthesis of Methyl Methacrylate from Propylene

REFERENCES

(5) J. F. Cordes and H. Günzler, Ber., 92, 1055 (1959); Z. Naturforsch, 15b, 682 (1960); German Pat. 1,093,350 (1960).