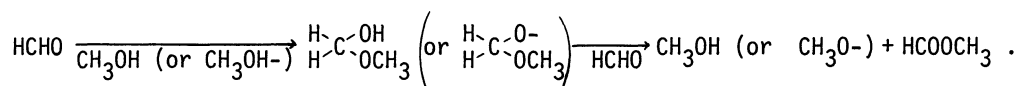


MECHANISM OF FORMATION OF METHYL FORMATE FROM FORMALDEHYDE OVER COPPER CATALYSTS

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Formation of methyl formate from formaldehyde was markedly enhanced by the presence of methanol over copper-silica and support-free copper catalysts. It was revealed that in the presence of methanol the formation proceeded through the route as



A number of patents have been recently published for the production of methyl formate by dehydrogenation of methanol.¹⁾ Although formaldehyde which is primarily formed by dehydrogenation of methanol is considered to be an intermediate species of methyl formate formation, it is still controversial whether methyl formate is produced primarily through the bimolecular reaction of formaldehyde $2\text{HCHO} \rightarrow \text{HCOOCH}_3$ or the reaction between formaldehyde and methanol.²⁻⁴⁾ In these connections, the reaction between formaldehyde and methanol as well as the dehydrogenation of methanol are carried out over copper-silica and support-free copper catalysts. We will show that the formation of methyl formate from formaldehyde is enhanced by the presence of methanol to an appreciable extent. By use of labelled compounds, it is revealed that when methanol is present, methyl formate is formed through the step involving the reaction between formaldehyde and methanol and no bimolecular reaction $2\text{HCHO} \rightarrow \text{HCOOCH}_3$ participates in the formation.

Copper-silica catalyst (10 wt% copper) was prepared by ion exchange between protons of surface hydroxyls of silica and tetrammine copper (II) cations.⁵⁾ The catalyst thus prepared was dried at room temperature overnight, calcined at 500°C in air for 3 hrs and subjected to the reduction in methanol-water mixture to metallic copper prior to the reaction. Experiments were carried out in a flow system for reactions between formaldehyde and methanol or ethanol, between methyl formate and methanol or ethanol, and dehydrogenation of methanol at atmospheric pressure. The products and reactants were analyzed by gas chromatography. Isotope distributions in the reactants and products were analyzed by GC-MS (JEOL JMS-D-300, Nippon Densi Co.). Formaldehyde was prepared by sublimation of paraformaldehyde. Alcohols and methyl formate used were vaporized in a nitrogen stream and were fed over the catalyst. Support-free copper catalyst was prepared by decomposition of basic copper carbonate and was subjected to the standard treatment as was done on copper-silica catalyst prior to the experiments.

When formaldehyde alone or the mixture of formaldehyde and methanol was admitted with the nitrogen stream over copper-silica catalyst, methyl formate was formed. Figure 1 shows the outlet partial pressure of methyl formate formed when either formaldehyde alone or the mixture was admitted over the catalyst at various temperatures. It is seen that the methyl formate formation

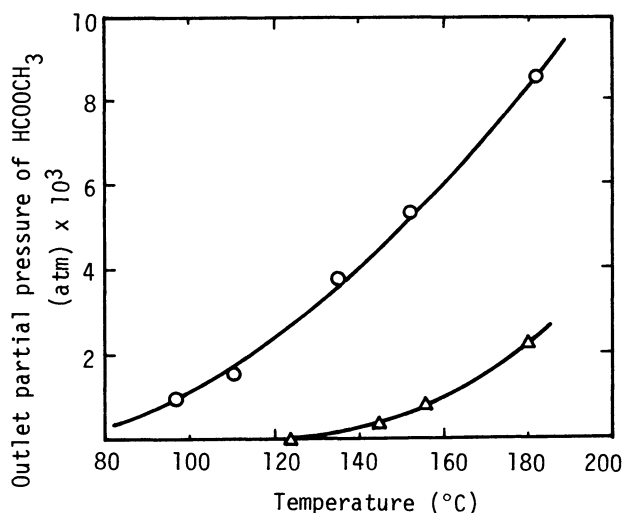


Figure 1. Methyl formate formation versus temperature

(-Δ-) : The reaction was carried out with formaldehyde alone. Inlet partial pressure : $P_{\text{HCHO}} = 0.011$ atm.

(-o-) : The reaction was carried out with the formaldehyde-methanol mixture. Inlet partial pressure : $P_{\text{HCHO}} = 0.011$ atm and $P_{\text{CH}_3\text{OH}} = 0.12$ atm.

Table 1. The ratio of formaldehyde consumed over methyl formate formed at steady state of the reaction between formaldehyde and methanol

Temperature (°C)	100	116	135	150	180
$\frac{\text{HCHO consumed}}{\text{HCOOCH}_3 \text{ formed}}$	1.9	2.0	1.9	1.6	1.2

is enhanced by 4 to 20 times in the presence of methanol. Table 1 shows the ratio of the amount of formaldehyde consumed over that of methyl formate formed when the reaction was carried out with the mixture at various temperatures. The ratio obtained approaches two at temperatures below 135°C. The formations of by-products such as hydrogen, carbon monoxide and carbon dioxide, and the consumption of methanol were practically negligible under these conditions. One molecule of methyl formate was, therefore, formed by consumption of two molecules of formaldehyde even in the presence of methanol at these temperatures. On the other hand, situation is complicated at higher temperatures. Methanol was found to be consumed and hydrogen was formed to an appreciable extent. It was likely that methanol admitted with formaldehyde was dehydrogenated by the reaction $2\text{CH}_3\text{OH} \rightarrow \text{HCOOCH}_3 + 2\text{H}_2$. In fact, when methanol alone was admitted over the catalyst, no reaction occurs at 135°C while at temperatures above 160°C the dehydrogenation was found to be appreciable. In these respects, the ratio (HCHO consumed / HCOOCH₃ formed) decreased with the temperature when the experiments were carried out at higher temperatures.

The reaction was carried out with formaldehyde-d₀ and methanol-d₃ CD₃OH at 130°C at which no dehydrogenation of methanol occurred. Figure 2 shows the mass spectra of methyl formate formed under these conditions. An intense peak due to the parent species is seen at $m/e = 63$, indicating that

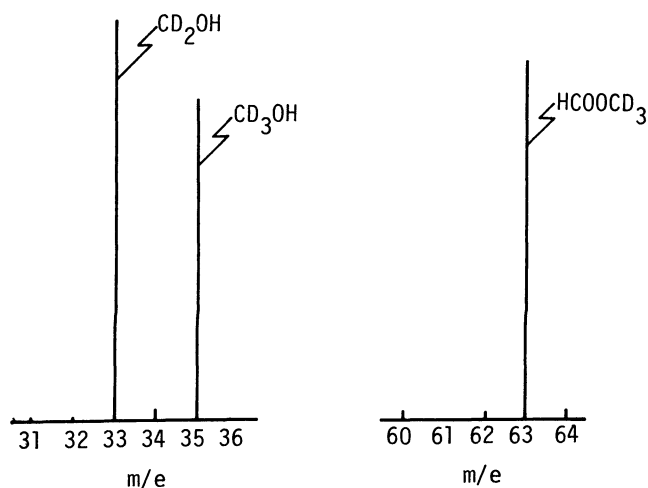
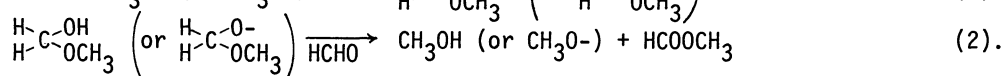
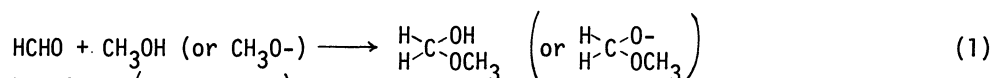


Figure 2. Mass spectra of methyl formate formed by the reaction between formaldehyde- d_0 and methanol- d_3 CD_3OH . Temperature : $130^\circ C$. Inlet partial pressures : $P_{HCHO} = 0.011$ atm. $P_{CD_3OH} = 0.017$ atm.

methyl formate- d_3 was predominantly formed. According to mass spectra of methyl formate obtained by Raalte and Harrison,⁶⁾ it gave intense peaks due to CH_3OH and CH_2OH fragments. The former fragment is formed by the selective reaction between formyl hydrogen and methoxy group of methyl formate, while the latter is formed by elimination of a hydrogen atom in methyl group of CH_3OH fragment.⁶⁾ In Fig.2 intense peaks due to these fragment ions are seen at $m/e = 35$ and 33 and these are, therefore, ascribed to CD_3OH and CD_2OH fragments, respectively. In these respects, it was concluded that $HCOOCD_3$ was predominantly formed when formaldehyde- d_0 was admitted with methanol- d_3 CD_3OH . Since it would be probable that methyl formate- d_0 was initially formed by the bimolecular reaction $2HCHO \rightarrow HCOOCH_3$ and transformed to $HCOOCD_3$ by the exchange reaction $HCOOCH_3 + CD_3OH \rightarrow HCOOCD_3 + CH_3OH$, the latter reaction was carried out at $130^\circ C$. However, the exchange of methyl group occurred less than 2% and was practically negligible. When the reaction was carried out between methanol- d_4 CD_3OD and formaldehyde- d_0 , methyl formate- d_3 $HCOOCD_3$ was formed predominantly. No bimolecular reaction $2HCHO \rightarrow HCOOCH_3$ was, therefore, involved in the methyl formate formation and methyl formate was formed primarily through the reaction between methanol and formaldehyde. In this case, a hydrogen atom of formaldehyde molecule was kept in formyl hydrogen in methyl formate molecule. When hydrogen was admitted with the mixture of formaldehyde and methanol, it was found that the methyl formate formation was unaffected by the presence of hydrogen. No hydrogen was consumed and no methanol was formed in any additional amount. This indicated that no hydrogenation of formaldehyde occurred with hydrogen in the course of the methyl formate formation. In these respects, it was most likely that when formaldehyde reacted with methanol, hemiacetal $\begin{matrix} H-C-OH \\ | \\ H-C-OCH_3 \end{matrix}$ or hemiacetal-like species $\begin{matrix} H-C-O- \\ | \\ H-C-OCH_3 \end{matrix}$ was primarily formed and hydrogen transfer occurred between either of the latter species and formaldehyde as



When the latter step proceeded at rapid rate compared to the former step, one molecule of methyl formate was formed by consumption of two molecules of formaldehyde although methanol participated in the reaction. In consistent with these reaction route, when ethanol was admitted with formaldehyde, ethyl formate and methanol was formed but the methyl formate formation was practically negligible. It was also confirmed that no reaction $\text{HCOOCH}_3 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{HCOOC}_2\text{H}_5 + \text{CH}_3\text{OH}$ occurred.

As for the formation of methyl formate by dehydrogenation of methanol, the reaction was extremely slow compared to that between methanol and formaldehyde. As has been concluded by Miyazaki and Yasumori,³⁾ the formation should be controlled by dehydrogenation of methanol to formaldehyde. When the dehydrogenation was carried out with CD_3OH at 180°C , methyl formate- d_4 DCOOCd_3 was formed exclusively. As these authors found, no hydroxyl hydrogen was involved in methyl formate. When the reaction was carried out with the mixture of CD_3OH and CH_3OH over copper-silica catalyst, formed methyl formates gave peaks at $m/e = 64, 63, 61$ and 60 in their mass spectra, indicating that methyl formates $-\text{d}_4, -\text{d}_3, -\text{d}_1$ and $-\text{d}_0$ were formed.⁷⁾ The formation rates of d_3 - and d_0 - species were found to be three to five times these of d_4 - and d_1 - species because of the isotope effect. As compared with the above results, methanol was first dehydrogenated to formaldehyde and the latter species transformed to methyl formate through the reactions (1) and (2). Therefore, formed methyl formates would be $\text{DCOOCd}_3, \text{HCOOCd}_3, \text{DCOOCH}_3$ and HCOOCH_3 species. A variety of reactions which were done over copper-silica were carried out over support-free catalyst. The results obtained were found to be practically the same as those obtained over the former catalyst. When the mixture of formaldehyde and methanol was admitted over silica support, no methyl formate was formed although methylal was detected. It was, therefore, concluded that the reactions which were studied in the present experiments proceeded over copper surface.

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