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# Isotopic Labeling Studies of the Mechanism of Dehydrogenation of Methanol to Methyl Formate over Copper-Based Catalysts

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Deuterium labeling has been used to study the processes occurring during the conversion of methanol to methyl formate over copper catalysts at 180–210°C and pressures of 0.3 to 1 atm. Deuterium substitution has a dramatic effect on rate, which decreases in the ratio 8 : 4 : 2 : 1 in the series $CH_3OH$, $CH_3OD$, $CD_3OH$, $CD_3OD$. This can be interpreted as the product of a primary kinetic isotope effect of four for replacement of $CH_3$ by $CD_3$ and a separate thermodynamic isotope effect of two on the concentration of a surface methoxy intermediate when OH is replaced by OD. The isotope effect provides strong support for a mechanism in which the slow step is the conversion of the methoxy group to formaldehyde. Reversibility of the conversion of methanol to methoxy is reflected by hydroxyl group exchange with $D_2$ at a rate much in excess of methyl formate production. $H_2/HD/D_2$ equilibration rates are still faster even though methanol coverages are high. The product distribution from $CD_3OD/CH_3OH$ mixtures shows that methyl formate formation involves transfer of an H or a D with a discrimination isotope effect of two. This rules out coupling by a methoxy plus CHO step but leaves unresolved the possibility that the formate is produced by a hemiacetal intermediate or by formaldehyde dimerization. This lack of resolution results from isotopic scrambling caused by concurrent transesterification reactions as demonstrated using $CD_3OH/CH_3OCHO$ mixtures.

## INTRODUCTION

Methanol can be catalytically converted to methyl formate either by direct dehydrogenation or by oxidative dehydrogenation. A number of oxide systems are active for the latter (*1*) and high yields are possible since there are no thermodynamic limitations. The disadvantage is that the hydrogen is eliminated as valueless water. Direct dehydrogenation

$$2CH_3OH \rightleftarrows CH_3OCHO + 2H_2 \quad (1)$$

yields hydrogen as well as the formate but equilibrium yields are below 50% under usable conditions. Copper-based catalysts appear to be uniquely effective for the system (*2–5*). In recent work (*4*) we have established that the activity of copper catalysts for the reaction is related to their exposed copper sites as assessed by the dissociative chemisorption of nitrous oxide. Thus it seems very likely that atoms of metallic copper are essential for activity. Indeed the inclusion of oxidic support components, while possibly desirable for stability reasons, seems to lower the intrinsic activity of the metal sites themselves (*4*).

The uniqueness of copper may be associated with its ability for sequential hydrogen removal stopping short of CO, i.e.,

$$CH_3OH \rightarrow CH_3O(a) + H(a) \quad (2)$$

$$CH_3O(a) \rightarrow CH_2O(a) + H(a) \quad (3)$$

$$CH_2O(a) \rightarrow CHO(a) + H(a) \quad (4)$$

Madix and co-workers (*6–8*) and Sexton (*9*) have shown that (2) is fast and reversible below room temperature on single-crystal planes while (3) requires tempera-

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tures in excess of 100°C. No evidence was found for formyl (CHO) species but there are suggestions for their existence in the hydrogenation of CO on Cu/ZnO (*10*).

In this work we have used deuterium labeling to study the characteristics of direct dehydrogenation over copper under conditions of practical interest. Our purpose has been twofold. First, some of our earlier work (*5*) had indicated that RO-transfer reactions of the transesterification type were possible and we wished to establish if they were an essential feature of the reaction. Second, we hoped to gain further insight into the sequence of individual steps which comprise a complex reaction such as this.

There have been two previous studies using isotopic tracers relevant to this work. Miyazaki and Yasumori (*11, 12*) followed the dehydrogenation of $CH_3OD$ over copper wire at pressures of less than 0.03 atm and temperatures from 250 to 310°C. Under these conditions the initial reaction products were HD and formaldehyde ($H_2CO$). They concluded that methyl formate-$d_0$ (i.e., $CH_3OCHO$) was then produced by formaldehyde dimerization (the Tischenko reaction)

$$CH_2O(a) + CH_2O(a) \rightarrow CH_3OCHO \quad (5)$$

Various exchange reactions yielding labeled products during the later stages of reaction were also established. Very recently Takahashi *et al.* (*13*) studied the reaction of formaldehyde-$d_0$ and methanol-$d_3$ ($CD_3OH$) at pressures of 0.01 to 0.02 atm over $Cu/SiO_2$ at 130°C. Methyl formate with isotopic composition indicative of $CD_3OCHO$ alone was produced. They concluded that, during methanol dehydrogenation, methyl formate would be similarly produced from methanol and formaldehyde via a surface hemiacetal intermediate—schematically

$$CH_3OH(a) + CH_2O(a) \rightarrow CH_3OCH_2OH(a) \quad (6)$$

$$CH_3OCH_2OH(a) + CH_2O(a) \rightarrow CH_3OCHO + CH_3OH \quad (7)$$

rather than by formaldehyde dimerization as claimed by Miyazaki and Yasumori (*11, 12*). This was supported by the observation that ethanol and formaldehyde yielded ethyl formate and *not* methyl formate under their conditions. They also found that the transesterification reaction between ethyl formate and methanol to yield methyl formate and ethanol

$$C_2H_5OCHO + CH_3OH \rightarrow CH_3OCHO + C_2H_5OH \quad (8)$$

was not significant under their conditions.

In both the above studies the conditions used were considerably different from those of practical interest (viz. 180–250°C and pressures near atmospheric). Our results indicate that the situation under these conditions is rather more complex than would be expected on the basis of this earlier work.

## EXPERIMENTAL

The flow reactor system and the general procedures were similar to those described earlier (*4*). In essence methanol was vaporized and passed over 0.1 to 2 g of catalyst contained in a stainless-steel U-tube immersed in a molten-salt bath maintained at constant temperature. In the present case the labeled methanols were fed from a syringe pump and a slow flow of nitrogen (and in some cases $H_2$ and/or $D_2$) used to assist its passage over the catalyst and through a trap cooled to −78°C to condense out the organic fraction. A sample of the gas leaving this trap was also collected during those experiments in which labeled feedstocks were used. The reactor itself operated at a total pressure of 1 atm of which the organic components comprised upwards of 0.3 atm.

The collected liquid fraction from each experiment was analyzed unseparated by NMR and mass spectrometry. $^1H$, $^2H$, and $^{13}C$ NMR spectra were obtained using a Varian XL 200 Fourier transform spectrometer. Resonances due to the four types of hydrogens (or deuterium) in methanol/methyl formate mixtures were quite well separated except for slight overlapping by $^{13}C$ satellites for which corrections were made as needed. A 20-s pulse delay was imposed to allow for relaxation and the relative areas of the four peaks in each spectrum obtained by integration. Normalization between $^1H$ and $^2H$ spectra was achieved by including a small amount of a 1 : 1 mixture of $C_6H_6$ and $C_6D_6$ as an internal standard in each analysis.

Mass spectra were recorded using an A.E.I. MS12 instrument. The vapor above a degassed sample of the collected liquid was admitted and the relative amounts of $d_0$ through $d_4$ methyl formates determined from parent peaks with $m/e$ from 60 to 64. Fragmentation was so small that the corrections needed for it were less than 1%. In a few cases the isotopic composition of the methanol was also determined. However, even with minimal ionization energies, significant corrections were necessary for fragmentation and the reliability was not as high. The relative amounts of $H_2$, HD, and $D_2$ in the gas samples collected were obtained with the same instrument. In this case the sensitivity for each component was not the same and there was some signal instability due to a marginal pumping speed and a slight but variable exchange in the instrument itself. These factors were allowed for by standardization using a mixture of $H_2$ and $D_2$ of known composition and averaging signals over a period of time.

The catalysts used comprised two tableted commercial copper chromites (Harshaw 1808 and 0203), a similar copper chromite powder prepared in this laboratory and a skeletal Raney copper. After reduction in $H_2$ at 250°C the 1808 catalyst was primarily copper metal on cupric chromite with some chromium oxide, while the 0203 catalyst contained more metal with cuprous chromite as the dominant oxide component (*14*). The laboratory-prepared sample was leached with concentrated HCl to remove copper and used as an oxide blank in some experiments. Composition, total areas, and copper metal areas (as determined by $N_2O$ chemisorption (*15*)), can be found in Table 3 or elsewhere (*14, 15*). We would have preferred to use the Raney copper throughout to avoid possible complications due to oxide but its initial deactivation is so rapid that experiments requiring relatively constant conversions were impractical. By contrast the 0203 copper chromite showed negligible deactivation over a period of hours. Labeled methanols were obtained from Merck Sharp & Dohme of Canada and each contained in excess of 99% D at the specified position. $D_2$ was obtained from Matheson and contained less that 1% H (as HD).

## RESULTS

The thermodynamics of methanol dehydrogenation places some constraints on the range of conditions usable for isotope experiments of the type planned here. At a total pressure of 0.35 atm (i.e., excluding the $N_2$ carrier) the equilibrium conversion of $CH_3OH$ is only 38.5% at 180°C. Estimates made using standard statistical thermodynamic methods show that deuterium substitution increases the potential conversion somewhat (e.g., to ~42% for $CD_3OD$). Most of the work has been done with conversions of 2–10% representing a balance between the desire to approach conditions of practical interest and facilitate analysis on the one hand and the need to avoid undue back reaction on the other.

### 1. *Products of $CH_3OD$ Dehydrogenation*

A preliminary experiment using $CH_3OD$ and the copper chromite catalyst 1808 was carried out to see if the conclusions reached by Miyazaki and Yasumori (*11*) using copper wire were directly transferable to these conditions. The results in Table 1 show a complex situation despite the relatively low conversion. The predominant methyl formate is $CH_3OCHO$ but there are also quite substantial numbers of molecules containing deuterium in methyl and aldehyde positions. Similarly there has been deuterium incorporation at the methyl position of un-

TABLE 1

Isotopic Composition from Conversion of $CH_3OD$ over Copper Chromite 1808 at 200°C[a]

| | By mass spectroscopy |
|---|---|
| Product methyl formate | |
| % $d_0$ | 83 |
| % $d_1$ | 15 |
| % $d_2$ | 2 |
| Product "hydrogen" | |
| % $H_2$ | 41 |
| % HD | 49 |
| % $D_2$ | 10 |
| D/(H + D) | 0.34 |
| Unreacted methanol (by NMR) | |
| % D in methyl | 2.2[b] |
| % D in "hydroxyl" | 85.3[b] |

[a] Catalyst (0.5 g), input gas flow = 134 $cm^3$ $min^{-1}$, $CH_3OD$ = 0.78 atm, $N_2$ = 0.22 atm, methanol conversion 1.7%.

[b] The starting methanol combined 0.18 and 99.8% D at these positions but some exchange at the OD position may have occurred during handling in this experiment.

reacted methanol beyond that expected for any back reaction and substantial loss of D from the OD group (some of this may represent losses in handling).

The most significant difference to the results of Miyazaki and Yasumori (*11*) is the formation of a randomized mixture of $H_2$, HD, and $D_2$ rather than HD alone. Initial production of all three species would not be too surprising under the conditions since the reaction is zero order (*4*) indicating high coverages and the probability of combining D (for example) from one molecule with the D from an adjacent molecule. This would be much less likely at the low pressures used by Miyazaki and Yasumori (*11*) when the reaction is first order and reacting molecules are widely spaced. Of course a statistical mixture could also arise from initial HD production and subsequent exchange. This possibility together with the origin of the other complexities noted above were investigated using in most instances the copper chromite 0203 which has a much higher ratio of copper metal to total area (66% versus 24%) than the 1808 catalyst.

### 2. *Equilibration of $H_2$ and $D_2$ during Reaction*

Several experiments were carried out in which 1 : 1 mixtures of $H_2/D_2$ were passed together with $CH_3OH$. As can be seen from Table 2 equilibration was near complete under conditions when methanol conversion was low. (Only at temperatures below 130°C did the extent of isotope equilibration fall below 50%.) It is clear that this process could account for the distribution observed from $CH_3OD$ even if HD was initially produced. Evidently rapid adsorption/dissociation/surface migration/recombination and desorption of hydrogen is possible even though methanol coverage is sufficiently high to result in zero-order kinetics. Perhaps the packing of methanol molecules leaves gaps sufficient to allow hydrogen adsorption or else not all surface sites are active for reaction and equilibration can take place on the remainder.

The finding of high $H_2/D_2$ equilibration rates on copper is not unique. Patterson *et*

TABLE 2

Hydrogen–Deuterium Equilibration in the Presence of Reacting $CH_3OH$ over Copper Chromite 0203 at 210°C[a]

| | |
|---|---|
| Product "hydrogen" | |
| % $H_2$ | 60.6 |
| % HD | 33.3 |
| % $D_2$ | 6.1 |
| D/(H + D) | 0.23 |
| Unreacted methanol | |
| % D in methyl | 1.2 |
| % D in "hydroxyl" | 9.9 |
| Product methyl formate | |
| % D in methyl | 1.6 |
| % D in aldehyde | 1.2 |
| Methanol conversion (%) | 3.7 |

[a] Catalyst (0.5 g), input flow of 407 $cm^3$ $min^{-1}$ comprising $CH_3OH$ = 0.61 atm, $H_2$ = 0.2 atm, $D_2$ = 0.19 atm, HD < 0.01 atm.

TABLE 3

Exchange between $CH_3OH$ and $D_2$ over Raney Copper, Copper Chromite 0203, and Leached Copper Chromite

| | Raney copper | Copper chromite 0203 | Leached copper chromite |
|---|---|---|---|
| BET area ($m^2g^{-1}$) | 18.6 | 16.3 | 60 |
| Copper metal area ($m^2g^{-1}$) | 18.0 | 10.8 | 0.9 |
| Temperature (°C) | 180 | 180 | 200 |
| Conditions | [a] | [b] | [c] |
| Methanol conversion (%) | 1.4 | 1.6 | nil |
| Product "hydrogen" | | | |
| % $H_2$ | 34 | 15 | not analyzed |
| % HD | 47 | 27 | |
| % $D_2$ | 19 | 58 | |
| D/(H + D) | 0.42 | 0.72 | |
| Unreacted methanol | | | |
| % D in methyl | 1.9 | 0.26 | <0.01 |
| % D in "hydroxyl" | 19.8 | 7.1 | 5.4 |

[a] Catalyst (2 g), (lined out in $CH_3OH$), input flow = 540 $cm^3$ $min^{-1}$ comprising $CH_3OH = 0.82$ atm, $D_2 = 0.18$ atm.

[b] Catalyst (1 g), input flow = 611 $cm^3$ $min^{-1}$ comprising $CH_3OH = 0.84$ atm, $D_2 = 0.16$ atm.

[c] Catalyst (0.2 g), input flow = 163 $cm^3$ $min^{-1}$ comprising $CH_3OH = 0.60$ atm, $D_2 = 0.4$ atm.

*al.* (*16*) observed significant equilibration in the presence of $C_4$ alcohols at 136°C. However, their catalyst contained 0.5% Ni and the extent to which this might have contributed to the activity was not established.

### 3. *Exchange between $D_2$ and $CH_3OH$*

The results of Table 2 indicate considerable incorporation of deuterium into the hydroxyl group but very little in the methyl group of unreacted methanol. (Table 1 shows similar loss of deuterium from $CH_3OD$.) The speed of this exchange process is best examined by experiments using $CH_3OH/D_2$ mixtures and the results of several such experiments are shown in Table 3. In each case the conversion of MeOH to MeOD substantially exceeds the conversion of methanol to methyl formate. However, this exchange is certainly a lot slower than the $H_2/HD/D_2$ equilibration rate since the distribution for the latter is near statistical with H/(H + D) very different to the OH/(OD + OH) ratio in the methanol. The nature of the sites responsible for $MeOH/D_2$ exchange is not clear. Exchange is certainly possible on copper since the Raney copper has substantial activity. However, there was also some exchange on the leached chromite catalyst, which has relatively few surface copper atoms as judged by nitrous oxide chemisorption and virtually no activity for methanol dehydrogenation. As a result, oxidic and acidic sites may contribute to the exchange activity.

Several mechanisms are conceivable for methanol exchange on copper itself but the reversible formation of a simple methoxy intermediate as demonstrated by Bowker and Madix (*8*) on Cu (110) seems the most likely, i.e.,

$$CH_3OH(a) \rightarrow CH_3O(a) + H(a) \quad (2)$$

$$CH_3O(a) + D(a) \rightarrow CH_3OD(a) \quad (2a)$$

The methoxy species has been observed directly in EELS work using copper single crystals (*9*).

The results in Table 3 also demonstrate some exchange into the methyl group but the D/(H + D) ratio is one-tenth or less of that in the hydroxyl position. The rate of atom exchange at the methyl position is therefore one-third or less that in the hydroxyl position and about half the reaction rate in the case of the 0203 catalyst. The origin of the incorporation of deuterium in the methyl group may be back-addition of $D_2$ to a formaldehyde intermediate. It is interesting to note that the relative extent of deuterium exchange at the two positions of methanol is quite different to the findings of Patterson *et al.* (*16*) for higher alcohols. They observed much more rapid exchange at the α-carbon of ethanol and 2-butanol than in the hydroxyl position, with little exchange at more remote positions.

### 4. *Kinetic Isotope Effect*

The reaction rates of $CH_3OH$, $CH_3OD$, $CD_3OH$, and $CD_3OD$ over the copper chromite 0203 were measured at low to moderate conversions for the temperature range from 180 to 200°C. The results are shown in

TABLE 4

Comparative Rates for Reaction of $CH_3OH$, $CH_3OD$, $CD_3OH$, and $CD_3OD$ over Copper Chromite 0203

| Methanol | Temperature (°C) | Methanol flow[a] | Methanol conversion[b] (%) | Rate ($10^5$ mol $s^{-1}$ $g^{-1}$) | Relative rate |
|---|---|---|---|---|---|
| $CH_3OH$ | 180 | 0.1 | 9.5 | 7.93 | 8.5 |
| | 190 | 0.1 | 15.1 | 12.6 | |
| | 200 | 0.1 | 20.3 | 16.9 | |
| $CH_3OD$ | 180 | 0.05 | 9.8 | 4.1 | 4.4 |
| | 190 | 0.05 | 14.0 | 5.8 | |
| | 200 | 0.05 | 18.3 | 7.9 | |
| $CD_3OH$ | 180 | 0.05 | 4.7 | 1.96 | 2.1 |
| $CD_3OD$ | 180 | 0.05 | 2.23 | 0.93 | 1.0 |

[a] Input flow of methanol in $cm^3$ (liquid) $min^{-1}$ over catalyst. Methanol pressure = 0.33 atm, $N_2$ = 0.67 atm.

[b] Experiments with labeled methanols generally involved replacement of $CH_3OH$ for a period of 30 min. During this period 5 to 8 determinations of the conversion of methanol were carried out and the average is as shown. The entire organic fraction leaving the reactor over the final 20 min was collected in a trap cooled to −196°C for analysis by mass spectrometery and NMR. Each run with a labeled methanol was bracketed by similar experiments with $CH_3OH$.

Table 4 and indicate an extremely large isotope effect. In fact the overall difference of a factor of eight in going from $CH_3OH$ to $CD_3OD$ is larger than any other of which we are aware for a heterogeneously catalyzed reaction at an equivalent temperature. It is larger than the maximum expected at 180°C (about 4.0) for a purely kinetic isotope effect originating from the zero-point energy difference for CH versus CD (or OH versus OD) bond breaking (*17*).

It appears that the rate differences observed arise from two contributions; a reduction by a factor of four resulting from substitution of $CH_3$ by $CD_3$ and a separate factor of nearly two when OH is replaced by OD. The former has also been noted in competitive experiments by Takahashi *et al.* (*13*). It is indicative of a primary kinetic isotope effect at the methyl group, i.e., the slow step in the reaction is the breaking of a carbon-to-hydrogen (or deuterium) bond (*17*). The most probable stage is during conversion of a methoxy intermediate to formaldehyde, e.g.,

$$CH_3OH(a) \rightleftarrows CH_3O(a) + H(a)$$
$$K_{OH} \text{ (or } K_{OD} \text{ for } CH_3OD \text{ or } CH_3OD) \qquad (2, 2a)$$

$$CH_3O(a) \rightarrow CH_2O(a) + H(a)$$
$$\text{slow } k_{CH} \text{ (or } k_{CD} \text{ for } CD_3O), \qquad (3)$$

where $k_{CH} = 4k_{CD}$ in the rate equations

$$\text{rate} = k_{CH}[CH_3O(a)] \quad \text{or} \quad \text{rate} = k_{CD}[CD_3O(a)].$$

The second factor of two for OH versus OD is then attributable to a thermodynamic isotope effect on the concentration of the methoxy species in the following way. (This argument in terms of kinetic and thermodynamic isotope effects is similar to that recently developed by Davis *et al.* (*18*) for skeletal isomerizations over Pt and by Kellner and Bell (*19*) for the Fischer–Tropsch synthesis.)

If reaction (2) is isolated then the relevant methoxy and hydrogen atom concentrations are equal and

$$[CH_3O](a) = (K_{OH} \cdot [CH_3OH(a)])^{1/2}.$$

The ratio of this concentration to that formed from $CH_3OD$ will be given by

$$\frac{[CH_3O(a)] \text{ ex } CH_3OH}{[CH_3O(a)] \text{ ex } CH_3OD} = \left[\frac{K_{OH}[CH_3OH(a)]}{K_{OD}[CH_3OD(a)]}\right]^{1/2}.$$

If the equilibrium constants are small then the surface concentrations of the two methanols can be assumed equal on the grounds of zero-order kinetics and the surface methoxy ratio reduces to $(K_{OH}/K_{OD})^{1/2}$. The equilibrium constant ratio can be expressed in terms of partition functions and zero-point energies as

$$\frac{K_{OH}}{K_{OD}} = \left(\frac{Q_H}{Q_D}\right) \cdot \frac{Q_{CH_3OD(a)}}{Q_{CH_3OH(a)}} \cdot \exp(-[(Z_{CuH}-Z_{CuD}) - (Z_{CH_3OD}-Z_{CH_3OH})]/RT)$$

where $Q_H$, $Q_D$, $Q_{CH_3OD}$, and $Q_{CH_3OH}$ are the partition functions of the adsorbed species and the $Z$'s are the corresponding zero-point energies. There are no terms in the methoxy species since it is the same from the two methanols. Evaluation of the above requires estimates for the vibrational frequencies for Cu–H and Cu–D which have not been measured.

Since the bond strength will certainly be less than that for adsorption on platinum the frequencies will be below those for Pt–H and Pt–D (2120 and 1585 $cm^{-1}$, respectively (*20*)). The likely extremes are CuH = 1500 $cm^{-1}$ (max), 600 $cm^{-1}$ (min), and CuD = 1100 $cm^{-1}$ (max), 440 $cm^{-1}$ (min). If adsorbed H and D are modeled as ideal two-dimensional gases (*18*) then $Q_H/Q_D$ (453 K) = 0.48 to 0.45. If surface motion is restricted these values will tend upwards. With the same model and using gas-phase rotational and vibrational constants $Q_{CH_3OD(a)}/Q_{CH_3OH(a)} \simeq 1.55$. Using the above estimates $Z_{CuH}-Z_{CuD} \sim 0.96$ to 2.34 kJ $mol^{-1}$ while $Z_{CH_3OD}-Z_{CH_3OH} = -6.4$ kJ $mol^{-1}$ (*17*). The exponential term is then 2.8 to 4.0 at 180°C. Overall the expected value for $K_{OH}/K_{OD}$ is 2.1 to 2.8 or more with the ratio of methoxy from $CH_3OH$ versus that from $CH_3OD$ upwards of 1.45. A similar argument will apply for the surface methoxy concentration starting from $CD_3OH$ as compared to $CD_3OD$. Thus in this system the thermodynamic and kinetic isotope effect are in the same direction and a very large overall rate difference in going from $CH_3OH$ to $CD_3OH$ to $CD_3OD$ can be explained.

### 5. *Transesterification*

The results of Table 1 also exhibit some introduction of deuterium into unreacted methanol. More significantly the percentages of D in the methyl formate and methanol are similar. This is indicative of a methoxy interchange process of the transesterification type, i.e.,

$$CH_2DOH + CH_3OCHO \rightleftarrows CH_2DOCHO + CH_3OH \quad (9)$$

The extent of this process over the copper chromite 0203 was checked by an experiment using a mixture containing $CH_3OCHO$ and $CD_3OH$ in the starting ratio 1 : 3. The results are shown in Table 5. Most significantly the methanol leaving the reactor contains increased hydrogen in the methyl group. Mass spectrometry showed that $CH_3$ and $CD_3$ were the dominant groups in both methanol and methyl formate. Since the D/(H + D) ratios in each are almost identical, near complete equilibrium for reaction (9) may be assumed.

TABLE 5

Methoxy Group Interchange between $CD_3OH$ and $CH_3OCHO$ during Reaction at 180°C

| | Input[a] | Output |
|---|---|---|
| Methanol | | |
| % D in methyl | 98.2 | 78.5 |
| % D in "hydroxyl" | Nil | 19.6 |
| Methyl formate | | |
| % D in methyl | Nil | 75.9 |
| % D in aldehyde | Nil | 17.1 |
| "Hydrogen" | | |
| % $H_2$ | — | 74.6 |
| % HD | — | 24.8 |
| % $D_2$ | — | 0.6 |
| D/(H + D) | — | 0.13 |

[a] Copper chromite 0203 (1 g), input flow 149 $cm^3$ $min^{-1}$ comprising $N_2$ = 0.69 atm, $CD_3OH$ = 0.23 atm, $CH_3OCHO$ = 0.08 atm. Methanol conversion ≃15%.

The above result is in contrast with the results of Takahashi *et al.* (*13*) who reported only 2% equilibration over copper on silica at 130°C but the difference may be explained in terms of the lower temperature and pressure they employed.

### *6. Mechanism of Methyl Formate Formation*

Processes by which methyl formate might be assembled can be divided into two distinct classes—those in which the methyl group is identical with that in the original methanol molecule, such as a reaction between methoxy and a formyl group

$$CH_3O(a) + CHO(a) \rightarrow CH_3OCHO \quad (10)$$

and those in which the methyl group is first broken down and later reformed, e.g., the Tischenko reaction

$$CH_2O(a) + CH_2O(a) \rightarrow CH_3OCHO \quad (5)$$

These classes are potentially distinguishable by experiments starting with $CH_3OH$ and $CD_3OH$ mixtures. The first can result in only $CH_3OCHO$ (M.W. = 60), $CH_3OCDO$ (61), $CD_3OCHO$ (63), and $CD_3OCDO$ (64); with the second, one expects $CH_3OCHO$ (60), $CH_2DOCDO$ (62), $CHD_2OCHO$ (62), and $CD_3OCDO$ (64). The latter expectation will be complicated by any transesterification which randomizes attachment of methyl to ester and hydroxyl functions thus giving the methyl formates with molecular weights of 61 and 63 as well. Nonetheless this situation is still distinguishable from the first category which, even with transesterification, cannot produce either of the $d_2$-methyl formates with M.W. = 62.

The hemiacetal mechanism as formulated by Takahashi *et al.* (*13*) is somewhat different. Starting with $CH_3OH$ and $CD_3OH$ the reactions include

$$CD_2O(a) + CH_3OH(a) \rightarrow CH_3OCD_2OH(a) \quad (6)$$

$$CH_3OCD_2OH(a) + CH_2O(a) \rightarrow CH_3OCDO(a) + CH_2DOH(a) \quad (7)$$

i.e., the initial methyl formates are identical to those for the formyl mechanism but methanols partially deuterated in the methyl group are predicted as well. In this case subsequent transesterification according to Eq. (9) will result in situations probably indistinguishable from the Tischenko reaction.

TABLE 6

Isotope Analyses for Reaction of 3 : 1 $CD_3OD/CH_3OH$ Mixture over Copper Chromite 0203 at 180°C[a]

| | |
|---|---|
| Methanol conversion (%) | 11 |
| Unreacted methanol (by NMR) | |
| % D in methyl | 73.6 |
| % D in hydroxyl | 72.5 |
| Methyl formate (by NMR) | |
| % D in methyl | 80.5 |
| % D in aldehyde | 35.3 |

Methyl formate (by mass spectroscopy)

| Combined | | Individual | b |
|---|---|---|---|
| % $d_0$ | 13.1 | $CH_3OCHO$ | 13.1 |
| % $d_1$ | 8.3 | $CH_3OCDO$ | 6.2 |
| | | $CH_2DOCHO$ | 2.1 |
| % $d_2$ | 5.2 | $CH_2DOCDO$ | 1.0 |
| | | $CHD_2OCHO$ | 4.2 |
| % $d_3$ | 50.2 | $CHD_2OCDO$ | 2.0 |
| | | $CD_3OCHO$ | 48.2 |
| % $d_4$ | 23.2 | $CD_3OCDO$ | 23.2 |

"Hydrogen" (by mass spectrometry)

| | |
|---|---|
| % $H_2$ | 38 |
| % HD | 40 |
| % $D_2$ | 22 |

[a] Catalyst (1 g), input gas flow = 152 cm$^3$ min$^{-1}$ comprising $N_2$ = 0.67 atm, $CD_3OD$ = 0.25 atm, $CH_3OH$ = 0.083 atm.

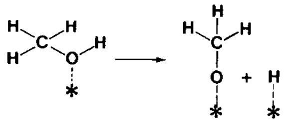
[b] Calculated assuming transesterification to be complete (see text).

The result of an experiment in which a mixture of $CH_3OH$ and $CD_3OH$ in the ratio 1 : 3 was passed over copper chromite 0203 is shown in Table 6. The mass spectral results clearly show the presence of $d_2$-methyl formates and mechanisms of the first type can be ruled out. However, as with Table 5, the %D in the methyl groups of methyl formate and methanol are so similar that transesterification must be close to equilibrium and the Tischenko and hemiacetal mechanisms cannot be distinguished.

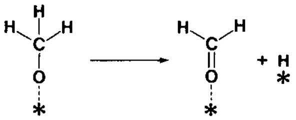
Detailed examination of the mass spectral data indicates that a discrimination isotope effect, of the kind identified by Adams and Jennings (*21, 22*), may be operative in the system. Thus, if all possible transesterification reactions are assumed complete with equilibrium constants of unity, then the amounts of $d_0$–$d_4$ methyl formates can be converted into percentages of each of the eight methyl formates. These are shown in Table 6, from which it is seen that the quantity with $CHD_2$ groups is about twice that with $CH_2D$ groups. As shown in the Appendix the presence of other exchange processes complicates interpretation of this result but if real it indicates that a discrimination isotope effect is involved during the intermolecular transfer (step 5 or 7) with H being transferred twice as often as D.

## DISCUSSION

The present results can be combined with preexisting information to form a rather detailed picture of this interesting example of $C_1$ chemistry. Methanol adsorbs weakly of copper (heat of adsorption ~20 kJ $mol^{-1}$ according to Borisov *et al.* (*23*) and Miyazaki and Yasumori (*11*)). Even so, calculations based on the adsorption parameters given by both these groups indicate that near complete monolayers would be possible under our conditions in accord with the observed zero-order kinetics (*4*). The results of Bowker and Madix (*8*) and Sexton (*9*) demonstrate unequivocally that removal of the hydroxyl proton is readily possible below 100°C. Sexton's EELS data also indicates that physically adsorbed methanol is relatively parallel to the surface whereas the $CH_3O$ group is more vertical. Hence dissociation may be written as

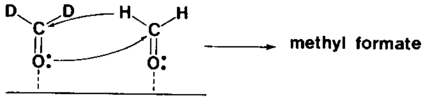


Apparently the extent of charge interchange with the surface during dissociation is quite small, since the dipole moment of the $CH_3O$ species is similar to that of methanol itself (*8*). Thus the surface species is better described as methoxy rather than methoxide. There is much evidence in this work and from work with single-crystal planes (*6–9*) that the dissociation is reversible and the slow step in dehydrogenation involves a second abstraction, i.e.,

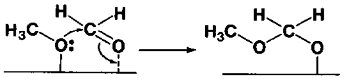


The mode of adsorption of formaldehyde is unknown but, based on ketones (*24*), one might expect bonding at an angle to a carbonyl lone pair with some weakening of the CO bond. Under some conditions, as with Raney copper (*4*) and with copper wire at low pressures (*11*), small amounts of formaldehyde can desorb and may be seen as a gas-phase product. However, coupling to give methyl formate, the more favored product thermodynamically, is more common.

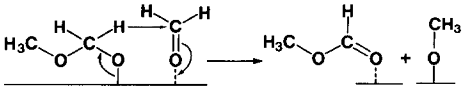
The experiments with $CD_3OD/CH_3OH$ mixtures demonstrate that a hydrogen-transfer step is involved in the process by which methyl formate is formed. With somewhat less certainty they point to the existence of a discrimination isotope effect during this step. If this is true then is readily explained in terms of the formaldehyde dimerization if written as



since there is competition for H or D transfer during the step in which the ester linkage is formed. It is rather less easy to explain in terms of the hemiacetal scheme of Takahashi *et al.* (*13*). That may be written with either methanol or methoxy as the species to which formaldehyde adds. The former seems more likely and, by analogy with solution reactions, might be written as

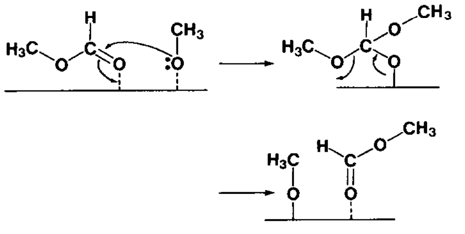


Conversion of this hemiacetal species to ester may then be written in an analogous fashion to the Cannizzaro reaction as a hydride-ion transfer to formaldehyde:



In this case formation of the ester linkage and hydrogen transfer take place in different steps and discrimination between H and D will not be possible unless there is reversibility of acetal formation. This may not be reasonable since it is after the slow step in the overall reaction. Thus, although the hemiacetal scheme seems analogous to chemistry of a well-established type, and Takahashi *et al.* (*13*) have provided good evidence for its existence under slightly different conditions, the isotope result is marginally more consistent with the Tischenko step. Copper is, of course, a good catalyst for formaldehyde dimerisation.

The two schemes for coupling could be readily distinguished by isotope measurements, in the way outlined earlier, in the absence of transesterification. In the same vein as the above this reaction may be written as



Transesterification, being commonly acid-catalyzed, might be thought a function of the catalyst support and indeed our earlier work (*5*) showed this can be so. However, copper alone was also a catalyst under conditions similar to those used here and, indeed, considerable conversion took place in an empty tube. Hence we are pessimistic about avoiding transesterification except at such low pressures that the overall course of dehydrogenation might also differ.

## APPENDIX

Competitive between H and D during the $CD_3OD/CH_3OH$ experiments can be specified in terms of the transferring species (H or D with $D/(H + D) = p$) and the recipient formaldehyde species ($CH_2O$ or $CD_2O$ with $CD_2O/(CH_2O + CD_2O) = q$). With both the Tischenko reaction and the hemiacetal mechanism the species from which the H or D is removed is also formaldehyde (or derived from it). With the above definitions one then expects in the product methyl formates

$$\frac{\mathrm{CDO}}{\mathrm{CHO} + \mathrm{CDO}} = p$$

and

$$\frac{\mathrm{CH_2D}}{\mathrm{CH_2D} + \mathrm{CHD_2}} = \frac{p(1 - q)}{p(1 - q) + q(1 - p)}.$$

Both these equalities will be quite unaffected by any transesterification. For the mass spectrometric data of Table 6 $p = 0.32$ and $q = 0.49$. (With the ratio $CD_3O/CH_3O$ of 3.0 in the starting methanols the expected value for $q$ is 0.43 given the measured kinetic isotope effect of four.)

The value $p = 0.323$ implies a discrimination isotope effect $k'_H/k'_D = 0.68/0.32 = 2.1$ for the H versus D transfer step. This conclusion should be regarded with some caution for the following reason. In the methyl formates *initially* formed we expect

$$\begin{aligned}\frac{\mathrm{CH_2D} + \mathrm{CHD_2}}{\mathrm{CH_3} + \mathrm{CH_2D} + \mathrm{CHD_2} + \mathrm{CD_3}}\ (\text{initial}) &= t\\ &= (1 - p)q + (1 - q)p\\ &= 0.495 \text{ in our case.}\end{aligned}$$

This value will be reduced by transesterification to an extent which depends on the overall methanol conversion. If the reaction were irreversible and transesterification is complete then it is possible to show that

$$\frac{CH_2D + CHD_2}{CH_3 + CH_2D + CHD_2 + CD_3} \text{(equilibrium)} = \frac{tx}{2 - x} = v,$$

where $x$ is the conversion. For the mass spectrometric data of Table 6 $v = 0.093$ requiring $x = 0.31$. The measured value of $x$ was 0.16. This difference reflects the presence of the same methyl group exchange processes noted in describing the results of Tables 2 and 3. Further calculations indicate that it is unlikely that this exchange is the sole cause of the twofold excess of $CHD_2$ over $CH_2D$ groups on which the inference of a discrimination isotope effect during hydrogen transfer is based. However, it is impossible to be absolutely certain on that point.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Ai, M., *J. Catal.* **83,** 141 (1983).
2. Charles, E., and Robinet, P., U.S. Patent 2,504,497.
3. Chono, M., and Yamamoto, T., *Shokubai* **23,** 3 (1981).
4. Tonner, S. P., Trimm, D. L., Wainwright, M. S., and Cant, N. W., *Ind. Eng. Chem. Prod. Res. Dev.* **23,** 384 (1984).
5. Evans, J. W., Casey, P. S., Wainwright, M. S., Trimm, D. L., and Cant, N. W., *Appl. Catal.* **7,** 31 (1983).
6. Wachs, I. E., and Madix, R. J., *J. Catal.* **53,** 208 (1978).
7. Wachs, I. E., and Madix, R. J., *Surf. Sci.* **76,** 531 (1978).
8. Bowker, M., and Madix, R. J., *Surf. Sci.* **95,** 190 (1980).
9. Sexton, B. A., *Surf. Sci.* **88,** 299 (1979).
10. Saussey, J., Lavalley, J. C., Lamotte, J., and Rais, T., *J. Chem. Soc. Chem. Commun.,* 278 (1982).
11. Miyazaki, E., and Yasumori, I., *Bull. Chem. Soc. Jpn.* **40,** 2012 (1967).
12. Yasumori, I., and Miyazaki, E., *Nippon Kagaku Zasshi* **92,** 659 (1971).
13. Takahashi, K., Takezawa, N., and Kobayaski, H., *Chem. Lett.* 1061 (1983).
14. Tonner, S. P., Wainwright, M. S., Trimm, D. L., and Cant, N. W., *Appl. Catal.* **11,** 93 (1984).
15. Evans, J. W., Wainwright, M. S., Bridgewater, A. J., and Young, D. J., *Appl. Catal.* **7,** 79 (1983).
16. Patterson, W. R., Roth, J. A., and Burwell, R. L., *J. Amer. Chem. Soc.* **93,** 839 (1971).
17. Ozaki, A., "Isotope Studies of Heterogeneous Catalysis." Academic Press, New York, 1977.
18. Davis, S. M., Gillespie, W. D., and Somorjai, G. A., *J. Catal.* **83,** 131 (1983).
19. Kellner, S., and Bell, A. T., *J. Catal.* **67,** 175 (1981).
20. Candy, J. P., Fauilloux, F., and Primet, M., *Surf. Sci.* **72,** 167 (1978).
21. Adams, C. R., and Jennings, T. J., *J. Catal.* **2,** 63 (1963).
22. Adams, C. R., and Jennings, T. J., *J. Catal.* **3,** 549 (1964).
23. Borisov, A. S., Tsvetkov, V. V., and Yagodovskii, V. D., *Russ. J. Phys. Chem.* **50,** 1288 (1976).
24. Sexton, B. A., Hughes, A. E., and Avery, N. R., in preparation.