JOURNAL OF CATALYSIS **100**, 28–38 (1986)

Hydrogenolysis of Methyl Formate over Copper on Silica

II. Study of the Mechanism Using Labeled Compounds

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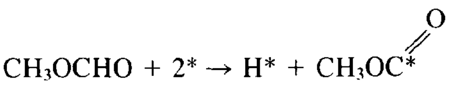
Received July 9, 1985; revised January 6, 1986

Deuterium labeling has been used to investigate processes occurring during the conversion of methyl formate to methanol over silica supported copper at 393 to 419 K. Unlabeled and labeled methyl formates (CH_3OCDO and CD_3OCHO) react with hydrogen and deuterium at identical rates. The product distribution is that expected for successive simple additions without exchange at methyl or aldehyde positions (e.g., the initial products of the reaction between CH_3OCHO and D_2 are CH_3OD and CHD_2OD). The only complication is a rapid transesterification equilibrium (e.g., $CH_3OCHO + CHD_2OD \rightleftharpoons CHD_2OCHO + CH_3OD$). Control experiments show that this process, and a similarly rapid $CH_3OH + D_2 \rightleftharpoons CH_3OD + HD$ equilibration, are catalyzed by copper and not the silica support. The mechanism suggested for hydrogenolysis involves formation of a surface hemiacetal species which, on cleavage of the C—O bond, gives surface methoxy groups and formaldehyde. It is unclear if the slow step is this bond cleavage or the addition step which forms the intermediate. During reaction between CH_3OCHO and H_2/D_2 mixtures equilibration to HD is 10 to 30 times faster than hydrogenolysis. Added CO inhibits both hydrogenolysis and equilibration but the latter is inhibited to a greater extent. Both effects can be explained in terms of the displacement of adsorbed hydrogen by adsorbed CO with equilibration being affected more because of its higher kinetic order in adsorbed hydrogen. The lower concentration of surface hydrogen concentration in the presence of CO also reduces the rate of hydrogenation of the formaldehyde intermediate causing its diversion into a polymeric by-product which poisons the catalyst.

INTRODUCTION

Mechanistic information about the hydrogenolysis of aliphatic esters to their corresponding alcohols, for which the preferred catalyst is copper (*1*), is quite scarce. Recently we have reported structure–reactivity relationships for a range of alkyl formates over copper chromite (*2*) and for some alkyl acetates on Raney copper (*3*). A major difference emerged in that the formates exhibited an increase in the hydrogenolysis rate with increasing molecular weight whereas with the acetates the reverse behavior was found. In addition the kinetics (3) of the gas-phase hydrogenolysis of ethyl acetate (first-order in hydrogen, −0.5-order in ethyl acetate) showed a completely different pattern compared with methyl formate (*4*) (zero-order in hydrogen, 0.39-order in methyl formate). Sørum and Onsager (*5*) have investigated the hydrogenolysis of methyl formate over copper chromite in the liquid phase. They proposed a reaction mechanism in which the dissociative chemisorption of methyl formate



$$CH_3OCHO + 2^* \rightarrow H^* + CH_3O\overset{O}{\overset{\|}{C}}{}^* \qquad (1)$$

is the first and rate-limiting step.

Since there have been many more mechanistic studies related to the hydrogenation of ketones (*6*) and especially acetone (*7*) than of esters, some comparisons of the two reactions may be helpful. Over most Group VIII metals the reaction between ac-

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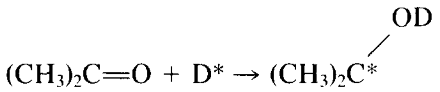
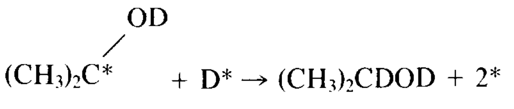
etone and hydrogen or deuterium involves the simple addition of two hydrogen atoms across the double bond of the keto form (6,7)



$$(\mathrm{CH_3})_2\mathrm{C{=}O} + \mathrm{D}^* \rightarrow (\mathrm{CH_3})_2\overset{\diagup\mathrm{OD}}{\mathrm{C}^*} \qquad (2)$$



$$(\mathrm{CH_3})_2\overset{\diagup\mathrm{OD}}{\mathrm{C}^*} + \mathrm{D}^* \rightarrow (\mathrm{CH_3})_2\mathrm{CDOD} + 2^* \qquad (3)$$

The experiments of Kemball and Stoddart (7) indicate that the second addition is usually rate determining. There is a kinetic isotope effect, k_H/k_D, of 2.09 with Pt, 3.63 with Ni, and 2.57 with Fe reflecting the need to break metal–hydrogen bonds of different strengths. However, there is no isotope effect with tungsten. It would appear that the above ideas may not apply in detail with copper since Patterson *et al.* (8) observed that the initial product of the reaction between deuterium and 2-butanone over copper powder containing 1% nickel was $CH_3CH_2CDOHCH_3$. This was tentatively interpreted as indicating that the second step (reaction 3 above) was not rate determining and that the hydrogen ending up in the hydroxyl originated from the 3 position of other molecules by an intermolecular disproportionation reaction.

In this study deuterated and undeuterated methyl formates have been reacted with hydrogen and/or deuterium. This ester is of particular interest since the same alcohol (methanol) is formed from two different functional groups and by using a label it is possible to decide how each reacts. The results are complementary to the *in situ* infrared measurements described in the companion paper (9). That work established the existence of a methyl formate species adsorbed on the copper and with surface concentration proportional to the hydrogenolysis rate. It also showed that polymerisation of by-product formaldehyde was the probable cause of catalyst deactivation in these systems.

EXPERIMENTAL

The copper-on-silica catalyst was prepared by ion exchange using Aerosil-type silica (Aerosil 300, Degussa A.G.) and a $Cu(NH_3)_4^{2+}$ complex. Details of the preparation method have been reported elsewhere (4). Some properties of the reduced catalyst are: BET-surface area by nitrogen adsorption: 247 m^2/g; copper content by atomic absorption spectroscopy: 8.2 wt%; copper surface area by nitrous oxide decomposition using a pulse chromatographic method (10): 6.7 m^2/g. An outstanding feature of this catalyst is that it exhibits no deactivation except in the presence of added carbon monoxide.

The flow reactor system used was essentially the same as in the previous study (9) but with the infrared cell/reactor replaced by an 0.6-cm-i.d. U-tube glass reactor. 0.5 g of the catalyst was loaded into the reactor and reduced with a 5% H_2/He mixture at 570 K. The reduction was completed in 100% hydrogen overnight (16 h). The reactor temperature was controlled to within ±0.5 K by a temperature controller connected to an iron–constantan thermocouple installed in the inner wall of the oven. The actual temperature of the catalyst was monitored by a second thermocouple located in an aluminum block which was in intimate contact with the reactor walls. The effluent gas stream was passed through a gas sampling valve and then through a trap cooled to 195 K to condense out the organic fraction. Samples of the gases leaving the cold trap were also collected during the experiments requiring $H_2/HD/D_2$ analyses.

Methyl formate (MeF)-d_0 (Ajax Chemicals Co.), MeF-d_1 (CH_3OCDO, 99 at.% D; Merck, Sharp & Dohme, Canada), and MeF-d_3 (CD_3OCHO, 99.6 at.% D, same supplier) were thermostated at 273 K in saturators. Depending on which reaction was studied, high-purity hydrogen (CIG, Australia), deuterium (Matheson), or a H_2/D_2 mixture of the composition H_2, 42%; D_2, 54.6%; and HD, 3.4% was passed through the appropriate saturator. Neglecting vapor pressure differences between the different methyl formates, a mole fraction of organic compound of 0.25 was calculated from vapor pressure data available for MeF-d_0 (*11*).

Most experiments with labeled formates were performed at 419 K with a total inlet gas flow rate of 40 cm^3(STP) min^{-1} when the product distribution of the hydrogenolysis reaction was of interest. At this temperature methyl formate conversion was higher than 25% resulting in product mixtures containing about equimolar amounts of methyl formate and methanol. When hydrogenolysis and H_2/D_2 equilibration were studied simultaneously, the same flow rate was used but the temperature was lowered to 393 K. Under these conditions, 10% of the methyl formate was converted and equilibration of the H_2/D_2 mixture was upward of 30%.

The collected liquid fraction from each experiment was analyzed by NMR and mass spectroscopy to determine position and amount of deuterium in the reaction products. ^1H and ^2H NMR spectra of the neat liquids were recorded with a Varian XL 200 Fourier transform spectrometer. A small amount (40 μl) of a 1 : 1 mixture of C_6H_6 and C_6D_6 was included in each sample as an internal standard to enable normalization between ^1H and ^2H spectra. An 18-s pulse delay sequence was used and spectra were recorded at 200 MHz for ^1H and 30.7 MHz for ^2H with a spectral width of 1000 and 3000 Hz for hydrogen and deuterium, respectively. Each spectrum showed five well-resolved peaks at 7.86 ppm (aldehyde), 7.15 ppm (benzene), 3.50 ppm (methyl group of methyl formate), 3.14 ppm (methyl group of methanol) with the OH (or OD) resonance ranging from 3.8 to 4.3 ppm depending on concentration. The relative areas of each peak were determined by integration. For each type of hydrogen, the fraction deuterium was calculated according to

$$\left(\frac{D}{D+H}\right)_i = \frac{AD_i/BD}{AD_i/BD + AH_i/BH} \quad (4)$$

where AD_i and AH_i are the areas of the peaks corresponding to deuterium or hydrogen in a particular position i and BD and BH are the areas of the C_6D_6 and the C_6H_6 peaks, respectively.

The overall chemical composition of the product mixture could be obtained similarly from the peak areas due to the $—CH_xD_{3-x}$ groups of methanol and methyl formate ($i = CH_xD_{3-x}$ in methanol, $j = CH_xD_{3-x}$ in methyl formate, x_M = mole fraction of methanol)

$$x_M = \frac{AD_i/BD + AH_i/BH}{\dfrac{AD_i + AD_j}{BD} + \dfrac{AH_i + AH_j}{BH}}. \quad (5)$$

This procedure was used to check for consistency with the composition obtained by gas chromatographic analysis. In general, compositions obtained by the two methods agreed within ±1%.

Mass spectra were recorded on a modified AEI MS20 180° deflection spectrometer with digital data readout. The instrument was equipped with a custom-made viscous leak inlet system especially designed to handle small quantities. Approximately 10 μl of the liquid product mixtures were cooled to 77 K and evacuated to a pressure of less than 1 Pa. The complete samples were then evaporated into the inlet system by removing the cooling medium and the inlet system connected to the MS. Analysis was performed at pressures of 10^{-5} Pa and with an ionization energy of 70 eV. The relative amounts of d_0 to d_4 methyl formates were determined from the peaks with m/e from 59 to 65 after making corrections for fragmentation and ^{13}C content. Fragmentation was experimentally determined for CH_3OCHO and the two labeled methyl formates used as reactants. After correction for incomplete deuteration of MeF-d_3 and MeF-d_1 the fragmentation pattern was

$$\text{MeF-}d_0,\ \text{MeF-}d_3\text{: } p - 1 : p : p + 1 = 1.3 : 100 : 2.4$$

$$\text{MeF-}d_1\text{: } p - 2 : p : p + 1 = 1.5 : 100 : 2.4$$

This indicates that the $p - 1$ and $p - 2$

signals are due to the abstraction of the hydrogen or deuterium in the aldehyde position. The overall degree of deuterium substitution for the $CH_{3-x}D_x$ group of methyl formate could be compared with the NMR results using

$$\left(\frac{D}{D+H}\right)_j = \frac{1 \times I(n+1) + 2 \times I(n+2) + 3 \times I(n+3)}{3 \times (I(n) + I(n+1) + I(n+2) + I(n+3))} \quad (6)$$

where $I(z)$ is the corrected intensity of the MS peak at $m/e = z$ and $n = 60$ for experiments with MeF-d_0 and MeF-d_3 and $n = 61$ when MeF-d_1 was used as a reactant.

The relative sensitivity of the mass spectrometer for H_2 and D_2 was determined by analysing a H_2/D_2 gas mixture made up with a precision capacitance pressure gauge. The factor obtained for $H_2 : D_2$ was 1 : 1.23. The sensitivity for HD was assumed to be between the value for H_2 and D_2.

RESULT

Control Experiments

Preliminary experiments using $CH_3OH + D_2$ were carried out to find exchangeabilities of methyl and hydroxyl hydrogens of methanol. Deuterium (30 cm^3 min^{-1}) was saturated with methanol-d_0 thermostated at 293 K which resulted in a methanol partial pressure of 9.1 kPa. In experiments at 419 K using the support alone there was no detectable exchange of hydrogens at either position in the methanol. However, the following compositions were obtained using Cu/SiO_2 at 419 K

$$\left(\frac{D}{D+H}\right) \text{hydroxyl} = 0.96, \qquad \left(\frac{D}{D+H}\right) \text{methyl} = 0.0097.$$

Thus copper is a very good catalyst for hydrogen exchange at hydroxyl groups. Indeed the D/(D + H) ratio for the hydroxyl group was greater than expected for complete equilibration with an equilibrium constant of unity. As explained later this reflects the presence of a thermodynamic isotope effect on the exchange process. By contrast, exchange at the methyl position was minimal. This was important since it meant that the isotopic composition produced at that position during MeF hydrogenolysis would be substantially retained.

Kinetic Isotope Effect

The possibility of a kinetic isotope effect was checked by measuring the rate of reaction of MeF-d_0, MeF-d_1, and the MeF-d_3 with hydrogen and deuterium under identical conditions (419 K, 0.5 g Cu/SiO_2, 30 cm^3(STP) min^{-1} H_2 or D_2 and 10 cm^3(STP) min^{-1} MeF). With MeF-d_0 the conversions were 24% with H_2 and 23.6% with D_2. Conversions for deuteration and hydrogenation of MeF-d_1 and MeF-d_3 were also the same within experimental error. According to the work of Kemball and Stoddart (7) with acetone an isotope effect would be expected only if cleavage of the metal-"hydrogen" bond was rate limiting. The absence of an effect indicates that either such a step is not rate determining or, alternatively, that the copper–hydrogen bond is so weak that the difference in zero point energy between CuH and CuD is too small to produce an effect.

Products of CH_3OCDO/D_2 and CD_3OCHO/H_2 Reactions

Analytical data for the MeF-d_1 + D_2 and MeF-d_3 + H_2 reactions are shown in Tables 1 and 2. The NMR results clearly show that for both experiments the methyl groups of unreacted methyl formate do not retain their identity. Rather they have undergone interchange with product methanol molecules since the D/(D + H) ratio is identical in each. This indicates that transesterification reactions of the type

$$CH_3OCDO + CH_xD_{3-x}OD \rightleftarrows CH_xD_{3-x}OCDO + CH_3OD \quad (7)$$

are at equilibrium with equilibrium constants of unity. Blank experiments using the silica support at 419 K and a 2 : 3 mix-

TABLE 1

Isotopic Composition from Reaction of CD_3OCHO with H_2 at 419 K (0.5 g Cu/SiO_2; MeF-d_3, 25 kPa; H_2, 76 kPa; flow rate, 40 $cm^3\ min^{-1}$)

NMR analysis		MS analysis	
i	$\left(\frac{D}{D+H}\right)_i$[a]	Methyl[b] groups of MeF	Relative amount (%)
MeF methyl	0.71	CH_3	29.3
MEF aldehyde	0.00	CH_2D	2.1
Methanol methyl	0.70	CHD_2	1.9
Methanol "hydroxyl"	0.00	CD_3	66.7
		$\left(\frac{D}{D+H}\right)_j$[c]	0.687

[a] From Eq. (4).

[b] Knowing aldehyde to be entirely CHO as per NMR analysis.

[c] From Eq. (6).

TABLE 2

Isotopic Composition from Reaction of CH_3OCDO with D_2 at 419 K (0.5 g Cu/SiO_2; MeF-d_1, 25 kPa; D_2, 76 kPa; flow rate, 40 $cm^3\ min^{-1}$)

NMR analysis		MS analysis	
i	$\left(\frac{D}{D+H}\right)_i$[a]	Methyl[b] groups of MeF	Relative amount (%)
MeF methyl	0.27	CH_3	71.9
MEF aldehyde	1.00	CH_2D	3.4
Methanol methyl	0.28	CHD_2	1.9
Methanol "hydroxyl"	1.00	CD_3	22.7
		$\left(\frac{D}{D+H}\right)_j$[c]	0.252

[a] From Eq. (4).

[b] Knowing aldehyde to be entirely CDO as per NMR analysis.

[c] From Eq. (6).

ture of CD_3OD and MeF-d_0 (15 $cm^3\ min^{-1}$) together with H_2 (30 $cm^3\ min^{-1}$) showed no detectable transesterification nor any hydrogenolysis. Rapid transesterification is well known during the hydrogenolysis of higher formates which produce two different alcohols (*2*). While no net transesterification is detectable when using CH_3OCHO and H_2 the isotope experiments clearly show that it is very rapid under hydrogenolysis conditions.

The existence of rapid transesterification coupled with the NMR result of absence of exchange at the aldehyde position greatly simplifies data treatment since it means that relative amounts of CH_3, CHD_2, CH_2H, and CD_3 can be calculated from the mass spectral data for MeF alone. As can be seen from Tables 1 and 2 the composition is >95% CH_3 plus CD_3. This is the expected result if the two reactions are

$$CH_3OCDO + 2D_2 \rightarrow CH_3OD + CD_3OD \quad (8a)$$

$$CD_3OCHO + 2H_2 \rightarrow CD_3OH + CH_3OH \quad (8b)$$

The different CD_3/CH_3 ratios in the two experiments reflect transesterification and the particular conversion levels. The small amounts of CHD_2 and CH_2D groups can be attributed to some exchange between methyl groups of methanol and H_2 (or D_2) as shown in the blank experiments together with a minor reaction pathway involving an intramolecular transfer.

Reaction of CH_3OCHO + D_2

The experiments above provide no information for or against the mechanism of Sørum and Onsager (*5*) which supposes that the initial step is detachment of the aldehyde hydrogen. A reaction of the type $CH_3OCHO + D_2$, in which the reducing agent and the species at the aldehyde position are isotopically different does provide a test. The results of such an experiment are shown in Table 3. The NMR results clearly show no exchange at the aldehyde position and equal D/(H + D) ratios in the methyl groups of methanol and MeF. The mass spectral results show no CD_3 groups

TABLE 3

Isotopic Composition from Reaction of CH_3OCHO with D_2 at 419 K (0.5 g Cu/SiO_2; MeF-d_0, 25 kPa; D_2, 76 kPa; flow rate, 40 cm^3 min^{-1})

NMR analysis		MS analysis	
i	$\left(\frac{D}{D+H}\right)_i^{a}$	Methyl[b] groups of MeF	Relative amount (%)
MeF methyl	0.13	CH_3	78.3
MeF aldehyde	0.004	CH_2D	3.4
Methanol methyl	0.13	CHD_2	18.3
Methanol "hydroxyl"	1.000	$\left(\frac{D}{D+H}\right)_i^{c}$	0.133

[a] From Eq. (4).

[b] Knowing aldehyde to be almost entirely CHO as per NMR analysis.

[c] From Eq. (6).

thus ruling out the Sørum and Onsager (5) scheme. The deuterium containing methyl groups are CHD_2 and CH_2D with the former six times as abundant. The major reaction is therefore

$$CH_3OCHO + 2D_2 \rightleftarrows CH_3OD + CHD_2OD \quad (9)$$

The CH_2D groups arise from exchange of product CH_3OD molecules with deuterium together with a minor reaction pathway. Direct confirmation of the methyl group composition was obtained by NMR using the DEPT pulse sequence (*12*) which discriminates between CHD_2 and CH_2D groups. The estimated ratio by this method was again 6.

Reaction of CH_3OCHO with H_2/D_2 Mixtures

To evaluate the relative rates of hydrogen adsorption/dissociation and hydrogenolysis, as well as the possible existence of discrimination isotope effects, an experiment was carried out with H_2/D_2 and CH_3OCHO over the Cu/SiO_2 at 419 K. Table 4 shows the composition of collected liquid and gas phases. The results show that H_2/D_2 exchange is close to equilibrium. Approximate calculations using the standard equation (*13*)

$$k_1 = \frac{F_H}{W} \ln \frac{[HD]_e - [HD]_o}{[HD]_e - [HD]} \quad (10)$$

where k_1 is the first-order exchange constant, F_H is feed rate of reducing agent, W is catalyst weight, and $[HD]_e$, $[HD]_o$, and $[HD]$ are equilibrium, initial, and measured $[HD]$ concentrations, showed that the rate of H_2/D_2 exchange was at least an order of magnitude faster than the hydrogenolysis reaction. Given that exchange must take place via adsorbed species, this means that the rate-determining step in the hydrogenolysis reaction is not the rate of hydrogen adsorption or dissociation. The $H_2/D_2/HD$ mixture after reaction was slightly deficient in deuterium with a small excess of hydrogen. This was compensated by a corresponding excess of deuterium in the "hydroxyl" group of methanol. Since exchange at this position is very fast, as shown in the blank experiments, this result implies that the equilibrium constant for the reaction

TABLE 4

Isotopic Composition from Reaction of CH_3OCHO with a $H_2:D_2:HD = 42:54.6:3.4$ Gas Mixture[a] (Conditions as in Table 1)

NMR analysis		MS analysis			
i	$\left(\frac{D}{D+H}\right)_i^{b}$	Methyl[c] groups of MeF	Relative amount (%)	$H_2/D_2/HD$	Relative amount (%)
MeF methyl	0.08	CH_3	79.0	H_2	22.5
MEF aldehyde	0.00	CH_2D	16.0	D_2	30.8
Methanol methyl	0.08	CHD_2	5.0	HD	46.7
Methanol "hydroxyl"	0.68	$\left(\frac{D}{D+H}\right)_j^{d}$	0.087		

[a] The corresponding equilibrium composition with an equilibrium constant of 3.7 (*13*) is $H_2:D_2:HD = 19.5:32.1:48.4$.

[b] From Eq. (4).

[c] Knowing aldehyde to be entirely CHO from NMR analysis.

[d] From Eq. (6).

$$CH_3OH + D_2 \rightleftarrows CH_3OD + HD \quad (11)$$

must be greater than unity. From the data in Table 4 a value of 3.27 was calculated. Calculations using standard methods of statistical mechanics (*14*) and available spectroscopic data gave an approximate value of 2.8 which is in good agreement.

By contrast to the "hydroxyl" position the deuterium content at the methyl position was less than expected. Thus if the input H_2 and D_2 reacted without an isotope effect the expected composition for the observed MeF mole fraction of 0.30 in the organics in the exit stream would be given by

$$\begin{array}{lll} & CH_3OCHO + 1.11D_2 + 0.89H_2 \rightarrow & \\ \text{Mole fractions} & 0.30 & \\ & H(D)OCD_{1.11}H_{1.89} + H(D)OCH_3 & (12) \\ & 0.35 \qquad\qquad 0.35 & \end{array}$$

and

$$\frac{D}{D + H} = \frac{0.35 \times 1.11}{3 \times 1.00} = 0.129.$$

The measured values are 0.081 by NMR and 0.087 by mass spectrometry. The discrepancy can only be explained by preferential incorporation of H into the methyl groups of methanol molecules during the course of the hydrogenolysis reaction.

At first sight this seems at odds with the absence of a measured kinetic isotope effect (as noted earlier) but can be explained in the following way. The ratio of the equilibrium constants for dissociative adsorption of hydrogen (K_H) and deuterium (K_D) can be calculated in the manner described by Davis *et al.* (*15*) if Cu—H and Cu—D vibration frequencies are known. While no direct information is available values of 1500 and 1100 cm^{-1} would seem reasonable (*16*). In this case if adsorbed H and adsorbed D are modeled as ideal two-dimensional gases (*15*) then $K_D/K_H = 0.4$ at 419 K. Regardless of total coverage the expected ratio of the surface coverages of deuterium and hydrogen will be $\theta_H/\theta_D = \sqrt{K_H P_{H_2}/K_D P_{D_2}} = 1.4$. If adsorbed H and D are assumed to react in a purely statistical way then the expected D/(D + H) in product methyl groups is reduced to 0.096. This is in much better agreement with the experimental results.

These conclusions can be summarized as follows. Hydrogen is expected to adsorb more strongly than deuterium so that in a competitive situation an excess of hydrogen is incorporated. However, when only H_2 (or D_2) is present no difference in rate is measured despite the stronger adsorption of hydrogen. These facts are reconcilable only if there is *total* coverage of the sites being used in each case. This explanation necessarily requires that the reaction order in hydrogen should be zero. We have previously shown this to be true with the catalyst used here (*4*).

Influence of CO on H_2/D_2 Equilibration and Hydrogenolysis

Carbon monoxide is an inhibitor for the hydrogenolysis reaction (*4*). The influence of 10% CO added to the reactant stream on the hydrogenolysis and the H_2/D_2 equilibration rates were studied at a reduced temperature of 393 K. Under these conditions it was possible to determine the rate of both reactions simultaneously. The results are compared in Table 5. With H_2/D_2 alone the product mixture was close to fully equilibrated (97% of possible). When H_2/D_2

TABLE 5

Effect of Carbon Monoxide on Rate of Hydrogenolysis of Methyl Formate and Rate of Equilibration at 393 K (0.5 g Cu/SiO_2; H_2/D_2, 30 cm^3 min^{-1}; MeF, 10 cm^3 min^{-1}; CO, 4 cm^3 min^{-1})

Reactants	k_1[a] (mol min^{-1} g^{-1})	$-r_{MeF}$ (mol min^{-1} g^{-1})
H_2/D_2	3.73×10^{-3}	—
H_2/D_2/MeF	2.56×10^{-3}	8.05×10^{-5}
H_2/D_2/MeF/CO	0.96×10^{-3}	4.70×10^{-5}
H_2/D_2/CO	1.75×10^{-3}	—

[a] From Eq. (10).

equilibration and hydrogenolysis were conducted simultaneously, the rate constant calculated according to Eq. (10) was about 70% of that without the organic compound. The actual H_2/D_2 exchange rate exceeded the hydrogenolysis rate by about a factor of 30.

Addition of CO reduced the speed of both reactions with the effect on the equilibration being larger than that on hydrogenolysis. With both methyl formate and CO present, the equilibration rate constant was reduced to 25% of the initial value. The hydrogenolysis rate under these conditions was 58% of the original value determined without CO. Inclusion of the CO alone with H_2/D_2 reduced the equilibration rate constant to less than half of the value measured with pure H_2/D_2. Comparison of lines 2 and 4 shows that CO inhibits equilibration more than MeF despite its lower pressure. Patterson *et al.* (*8*) have reported a reduction in the rate of formation of HD on a copper catalyst at 408 K to 20% of its original value when 13% acetone, 2-butanol, or tert-butyl alcohol were added to a H_2/D_2. In our experiments the rate of exchange was depressed to a lesser extent by methyl formate alone. However, when CO and methyl formate were present the reduction in the equilibration rate was about the same as in Pattersons' (*8*) results.

It is interesting to note that in the presence of CO the rate of equilibration was reduced more than the hydrogenolysis rate. This result can be explained by comparing two possible rate expressions for the two reactions. The rate of HD production can be taken as proportional to the coverages of the copper surface by hydrogen (θ_H) and deuterium (θ_D) according to a Bonhoeffer–Farkas mechanism (*13*)

$$r_{HD} = k_1'\theta_H \cdot \theta_D. \qquad (13)$$

For the speed of the hydrogenolysis reaction, the following expression applies if the surface reaction between methyl formate and hydrogen is limiting.

$$-r_{MeF} = k\theta_{MeF} \cdot \theta_H. \qquad (14)$$

It is obvious that a decrease in hydrogen (deuterium) coverage affects the rate of equilibration much more than the hydrogenolysis rate since the former is second-order in "hydrogen" coverage whereas the latter is first-order.

Competitive adsorption of methyl formate and carbon monoxide has been studied by *in situ* infrared spectroscopy (*9*). In those experiments it could be shown that methyl formate displaced adsorbed CO and not vice versa. Thus addition of CO cannot reduce the rate of the hydrogenolysis reaction by decreasing the amount of methyl formate adsorbed. On the other hand hydrogen is weakly adsorbed compared with CO and its coverage of the surface is severely affected when CO is present. When the hydrogenolysis of methyl formate was conducted without CO in the feed, a zero-order dependency with respect to the hydrogen partial pressure was found (*4*). In this case the overall rate only depends on the amount of methyl formate adsorbed. When CO is added, the fraction of the surface not occupied by methyl formate is preferentially covered by CO and the overall rate becomes a function of θ_H as well.

The following model is capable of describing all the experimental information. The basic assumptions are that methyl formate can only cover a fraction of the surface because of steric effects and that hydrogen and CO compete for the spaces left between the methyl formate molecules. In this sense, the adsorption of methyl formate and of hydrogen and CO can be described as proceeding on two different centers.

These assumptions lead to a Langmuir–Hinshelwood expression for the hydrogenolysis rate (from Eq. (14)) of the form

$$-r_{MeF} = k \cdot \frac{K_{MeF}P_{MeF}}{(1 + K_{MeF}P_{MeF})} \cdot F \cdot \frac{\sqrt{K_{H_2}P_{H_2}}}{(1 + \sqrt{K_{H_2}P_{H_2}} + K_{CO}P_{CO})} \qquad (15)$$

where the K's represent adsorption coefficients and F is the fraction of the surface available for adsorption of CO and H_2 as a consequence of not being occupied by MeF. According to this expression, at constant MeF pressure the reaction rate would be independent of hydrogen partial pressure when the CO partial pressure is small. At high partial pressure of CO, however, the reaction rate would be reduced due to adsorption of CO in preference to H_2 and the relationship between reaction rate and gas-phase concentrations is complex.

MECHANISM

In purely formal terms conversion of methyl formate to two methanol molecules requires the addition of four hydrogens (two to carbon and two to oxygen) and cleavage of a C—O bond. One would like to be able to specify the order of these five steps and to identify the slow step. This work, in conjunction with our earlier spectroscopic results (*9*), provides the following definitive information

(i) The reaction rate is proportional to the concentration of a surface species with a carbonyl group, probably intact methyl formate. Thus this species, or another in equilibrium with it, is involved in the rate-determining step.

(ii) The product distributions from the experiments with labeled methyl formates and MeF-d_0 + D_2 preclude processes requiring breaking of carbon to hydrogen bonds.

(iii) H_2/D_2 exchange is much more rapid than MeF hydrogenolysis so the latter is not limited by the rate at which adsorbed hydrogen atoms can be formed.

(iv) Exchange of the hydrogen in the OH groups of methanol is very rapid so that it is unlikely that the rate-determining step involves addition of a hydrogen atom to a surface species bound to copper via an oxygen atom.

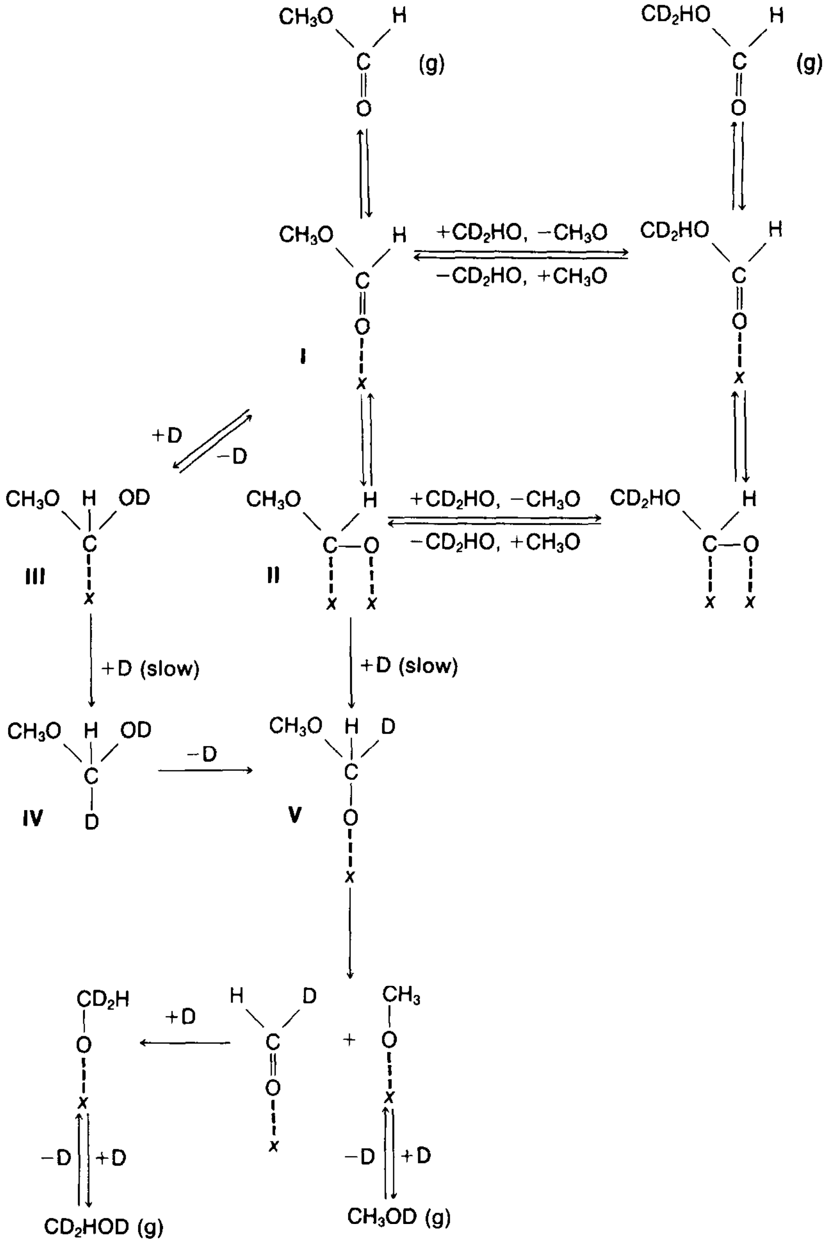
(v) There is no kinetic isotope effect for deuterium substitution in the reducing agent or at either carbon in MeF.

(vi) Transesterification is a rapid process.

The reaction scheme shown below is consistent with these findings. The central feature is the hemiacetal-like species (**V**) formed either by successive addition of deuterium to the oxygen and then the carbon of the carbonyl group to form the hemiacetal itself (**IV**), or, more likely, by a single addition to the carbon atom of associatively adsorbed MeF (**II**). Whichever pathway operates the addition to the carbon must be irreversible to accommodate point (ii). Cleavage of **V** yields methoxy groups, which are readily converted to methanol, and formaldehyde which is itself further hydrogenated. There is no direct evidence in respect of species **II** and **III**. For acetone adsorbed on Ni/SiO_2 Young and Sheppard (*17*) identified an infrared band characteristic of intact acetone, equivalent to species **I**, at 1685 cm^{-1}, and others at 2967, 2930, and 2881 cm^{-1} which they attributed to an associatively adsorbed species like **II**. After allowing for different extinction coefficients they claimed that the latter species was the more abundant. Given the much lower activity of copper toward carbon–oxygen multiple bonds a lower concentration of an associatively adsorbed species would be expected. Infrared spectra under MeF hydrogenolysis conditions show only adsorbed **I** (*9*). In terms of the reaction scheme the intermediates **II** and **III** need be present in nothing more than trace amounts.

The reaction scheme has the particular virtue of explaining both effects observed when carbon monoxide is included in the feed. These are direct rate inhibition (*4*), which is attributable to CO lowering the concentration of surface hydrogen required for the irreversible addition step, and slow poisoning due to the buildup of a formaldehyde polymer. The latter is to be expected since the lower concentration of surface hydrogen when CO is present would decrease the rate of formaldehyde hydrogenation and increase the probability of its diversion into a side reaction.

One point requiring some further elabo-



Reaction of CH_3OCHO with D_2 over copper

ration is the absence of a kinetic isotope effect when H_2 is replaced by D_2. Over Group VIII metals the rate of reaction of acetone with H_2 is commonly two to four times higher with H_2 than with D_2 (*7*). This is attributed to the need to break a bond to the metal surface when hydrogen (or deuterium) is transferred to the carbonyl carbon in the rate-determining step. The higher zero point energy of hydrogen compared to deuterium gives an isotope effect of the usual type (*13*). The absence of a similar effect with methyl formate might suggest that the slow step is something other than hydrogen addition such as cleavage of **V**, or perhaps formation of the associatively species **II** from **I**. However, it may be simply that CuH and CuD bonds are so weak that the difference in zero point energies between them is too small to confer a significant rate difference. It may be noted here that if C—O cleavage were rate limiting then the overall reaction is in effect two separate double-bond hydrogenations, while if addition and cleavage are concerted so that species **V** becomes a transition state between **II** and products then it is a true hydrogenolysis. In the latter case, no isotope effect would be expected on deuterium substitution if the barrier to be overcome was primarily determined by the requirements for breaking the CO bond.

The scheme for methyl formate conversion does not include transesterification as an integral part. That reaction probably proceeds by interchange between surface methoxy groups and the methoxy groups of methyl formate adsorbed as **I** or **II** as described in more detail elsewhere (*16*) and as indicated in the right-hand part of the reaction scheme. It is analogous to the standard base-catalyzed ester interchange reaction (*18*).

The slowness of methyl formate hydrogenolysis compared to this step indicates that either addition of hydrogen to the carbonyl carbon is much more difficult than that of a methoxy group or that attachment of hydrogen does not facilitate O—C cleavage so that step becomes limiting.

The reaction scheme suggested for the reverse methanol-to-methyl formate conversion (*16*) closely resembles the one presented here but with the slow step being conversion of methoxy groups to formaldehyde. Of course near equilibrium the slow steps in each direction must be the same. However, the hydrogen pressures present during methyl formate hydrogenolysis are so much greater than equilibrium that this need not apply here. The earlier work ruled out formation of methyl formate by addition of methoxy groups to formyl (CHO) species. Similarly, direct cleavage of CH_3OCHO to CH_3O and CHO is unlikely here especially with the high hydrogen pressures. However, under some conditions and with some copper catalysts CO is a significant product (*4*, *19*). This may reflect direct cleavage and/or abstraction of the aldehyde hydrogen as in the base-catalyzed decarbonylation reaction (*20*).

ACKNOWLEDGMENTS

Funding for this project under the Australian Research Grants Scheme is gratefully acknowledged. Preliminary isotope experiments on the system were carried out by J. W. Evans.

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