

Preliminary communication

HOMOGENEOUS CATALYSIS OF THE HYDROGENOLYSIS OF METHANOL USING IODIDE-PROMOTED RHODIUM CATALYSTS

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(Received June 17th, 1982)

Summary

In the presence of hydrogen, methane can be a co-product in the carbonylation of methanol to acetic acid using iodide-promoted homogeneous rhodium catalysts. The methane is formed by hydrogenolysis of methanol. Rhodium(III) species are implicated in catalysis of methane formation.

Iodide-promoted homogeneous rhodium catalysts are used commercially for the production of acetic acid by carbonylation of methanol [1,2] (eq. 1):



The water gas shift reaction (WGSR) can also be effected using an essentially similar catalyst system [3,4] (eq. 2). It is less widely known that iodide-



promoted rhodium catalysts will also promote the hydrogenolysis of alcohols to alkanes [5] (eq. 3).



We wish to report preliminary results on the hydrogenolysis of methanol to methane according to eq. 3, together with some indications of the relationships of this reaction to the carbonylation and water gas shift reactions.

The hydrogenolysis of methanol is readily carried out in aqueous solutions containing hydrogen iodide, using a soluble rhodium catalyst such as the diacetate. Supercritical pressures of hydrogen, together with significant partial pressures of carbon monoxide, are necessary for the reaction to proceed, and carbonylation of methanol (eq. 1) is always a competing reaction. No methane is produced in the absence of rhodium, ruling out a simple HI-

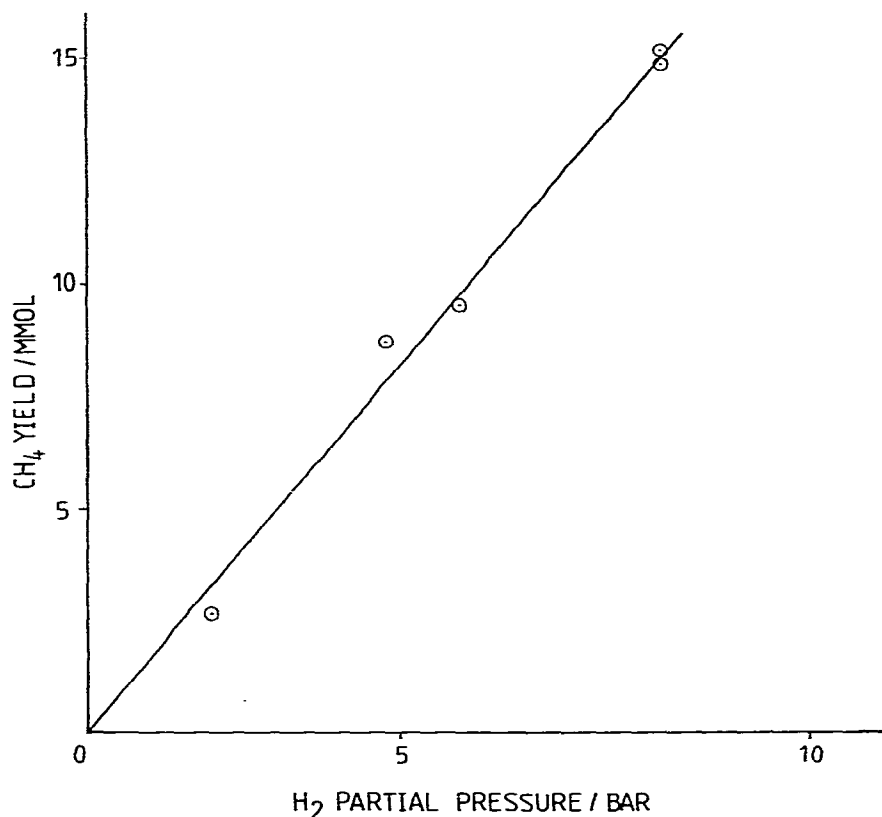


Fig. 1. Effect of H₂ partial pressure on CH₄ yield. Reaction conditions: 125°C, 5.1 bar CO; 210 mmol H₂O, 78 mmol CH₃OH, 6 mmol HI, 245 mmol C₂H₅CO₂H, 0.1 mmol Rh₂(OAc)₄. Reaction time 3.5 h.

catalysed mechanism [6]. Hydrogenolysis of CD₃OD with H₂ in H₂O solution produces only CD₃H, ruling out methanation of CO as a source of methane. We have investigated the hydrogenolysis of methanol under two different regimes of temperature and pressure.

Results of experiments at relatively low temperature and CO partial pressure (125°C, 5.1 bar CO) are displayed in Fig. 1 and 2. Under these conditions carbonylation of methanol to acetic acid and hydrogenolysis to methane proceed at comparable rates. The rate of carbonylation is, however, only ca. 20% of that found under the same conditions when hydrogen is not present.

The yield of methane increases approximately linearly with hydrogen partial pressure (Fig. 1). The effect of iodide concentration (Fig. 2) is more complex, with the yield of methane passing through a maximum at ca. 0.5 mol l⁻¹ HI.

At higher temperatures and CO partial pressures (170°C, 34 bar CO), carbonylation of methanol generally proceeds at the expected rate [7] and no methane is produced at hydrogen partial pressures of up to 8 bar. Methane can, however, be produced in such circumstances if the water gas shift reaction is allowed to operate for a period before the methanol is added to the reaction mixture. Thus if, under these conditions with no hydrogen initially present, the WGSR is allowed to proceed until a hydrogen partial pressure of ca.

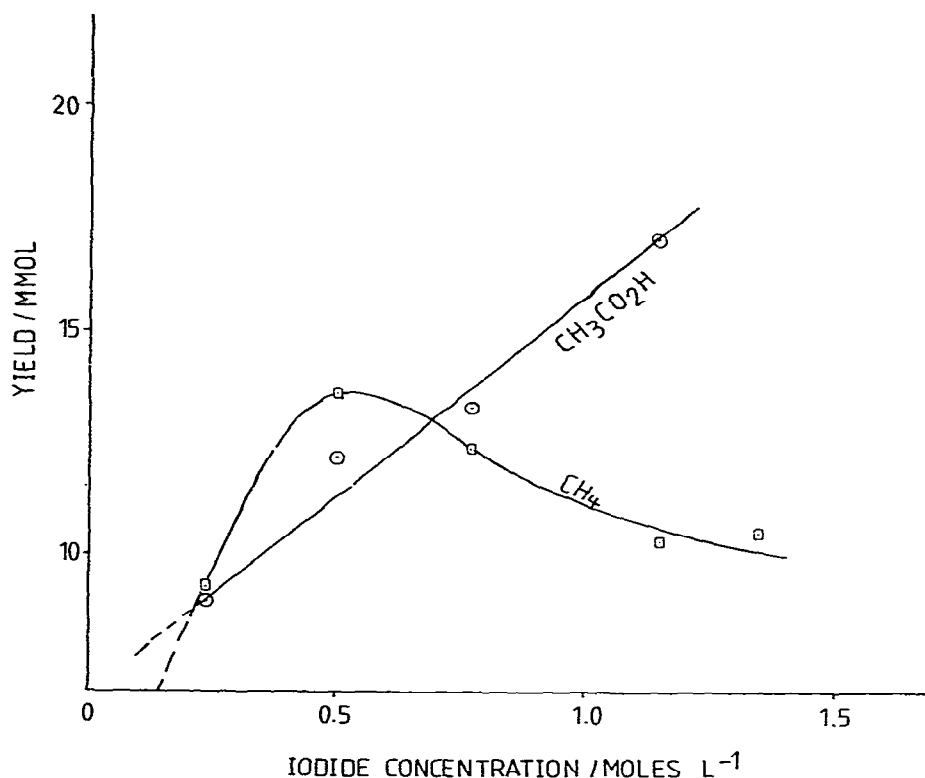


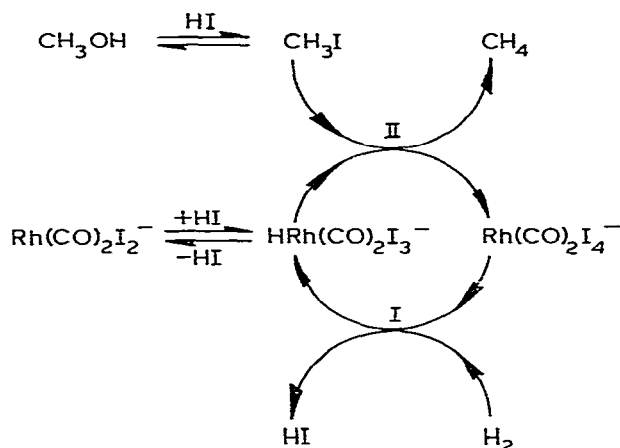
Fig. 2. Effect of iodide concentration on yields of $\text{CH}_3\text{CO}_2\text{H}$ and CH_4 . H_2 partial pressure 5.1 bar. Other conditions as for Fig. 1, but with amount of HI varied.

4 bar is attained, and the methanol introduced only at this point, methane production and carbonylation proceed in parallel, and with the rate of carbonylation reduced below that expected. We interpret this as meaning that prior operation of the WGSR sets up a catalytic regime under which hydrogenolysis is favoured, and carbonylation is inhibited.

We have no definitive data regarding the rhodium species in solution during a methane-forming reaction, but the dark colour of the solutions is indicative of the presence of rhodium(III) species. In contrast, reaction solutions in which carbonylation is proceeding in the absence of hydrogenolysis show the pale straw colour of the $\text{Rh}(\text{CO})_2\text{I}_2^-$ ion. It is noteworthy that rhodium(III) species are known to predominate under WGSR conditions at 170°C [3,4].

A number of mechanisms could be proposed for the hydrogenolysis reaction. We suggest that shown in Scheme 1 as being one that fits our observations.

The dependence of methane yield on hydrogen partial pressure (Fig. 1) suggests that Step I is rate limiting. The inhibition of hydrogenolysis at high iodide levels suggests, moreover, that this step is equilibrium limited. This latter point derives some support from the observation [8] that $\text{Rh}(\text{CO})_2\text{I}_2^-$ is oxidised to $\text{Rh}(\text{CO})_2\text{I}_4^-$ by aqueous HI with the evolution of H_2 , probably by the following sequence, which has been postulated [9] as an equilibrium (eq. 4):



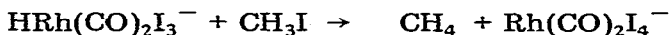
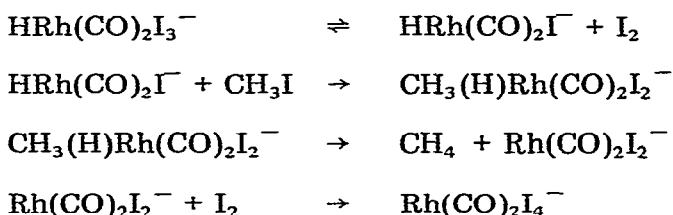
Scheme 1 Proposed catalytic mechanism

(eq. 4):



If Step I in Scheme 1 is indeed rate limiting, the standing concentrations of $\text{HRh}(\text{CO})_2\text{I}_3^-$ and of $\text{Rh}(\text{CO})_2\text{I}_2^-$ will also be small, according to the equilibrium of eq. 4. As $\text{Rh}(\text{CO})_2\text{I}_2^-$ is the key species in the carbonylation reaction, [1,2] this would explain the inhibition of carbonylation under conditions of concurrent carbonylation and hydrogenolysis.

Step II of Scheme 1 has been written as a simple bimolecular reaction between $\text{HRh}(\text{CO})_2\text{I}_3^-$ and CH_3I . A multi-step process involving oxidative addition of CH_3I to a rhodium(I) hydride is also conceivable:



In this modification of the scheme, the reductive elimination of methane from a methyl metal hydride, known to be a very fast reaction [10], presumably competes with methyl migration to give an acetyl complex (also known to be very fast with rhodium carbonyl iodide derivatives [1]).

Acknowledgements. We wish to thank Professor P.M. Maitlis for helpful discussions throughout the course of this work and also BP Chemicals Ltd. for allowing publication of this account.

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