

## Mechanism of the Catalytic Decomposition of Methanol on Gold Filaments

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*Summary* The mechanism of the catalytic decomposition of methanol on gold has been investigated using deuteriated methanol; the primary products of  $\text{CH}_3\text{OD}$  decomposition are  $\text{CHDO}$  and  $\text{H}_2$  and further reaction leads to mainly  $\text{HCHO}$ ,  $\text{HD}$ , and  $\text{CO}$ .

THE initial products of methanol decomposition on gold are formaldehyde and hydrogen;<sup>1</sup> the formaldehyde formed subsequently decomposes to carbon monoxide. In the present work deuteriated methanol has been used to elucidate the mechanism of the overall decomposition on gold filaments.

The reaction was carried out in a static system, with initial  $\text{MeOD}$  pressures of *ca.*  $5 \times 10^{-2}$  Torr (1 Torr =  $133.3 \text{ N m}^{-2}$ ). Two Spec-pure gold filaments each 0.2 mm

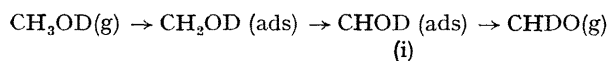
diameter and 40 cm long were supported by glass-covered tungsten leads. The decomposition was studied over the temperature range 950–1200 K. A small sample of the gases in the reaction vessel was continuously withdrawn through a capillary, and analysed using a quadrupole (EAI 250) mass spectrometer.

Analysis of the gas phase during the decomposition of  $\text{MeOD}$  at 1000 K is shown in the Figure. The initial reaction results in the formation of  $\text{CHDO}$  and  $\text{H}_2$ , indicating that the first step in the catalytic decomposition is the cleavage of carbon–hydrogen bonds, and not the oxygen–hydrogen bond as suggested previously<sup>2–4</sup> for methanol decomposition on other metals. The  $\text{CO}$ , which is detected at a later stage, results from the readsorption and subsequent decomposition of formaldehyde. Simultaneously

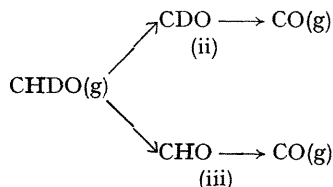
with the CO formation non-deuteriated formaldehyde, CH<sub>2</sub>O, is observed. The mechanism of CH<sub>2</sub>O formation was investigated by decomposing CD<sub>3</sub>OD on gold in the presence of CH<sub>2</sub>O. Both CHDO and the expected CD<sub>2</sub>O were formed, showing that either hydrogen–deuterium exchange occurs between the formaldehyde species, or reaction takes place between formaldehyde and methanol. The product distribution (Figure) suggests that the latter is the more likely, since hydrogen–deuterium exchange between two CHDO molecules would be expected to result in the formation of equal concentrations of CH<sub>2</sub>O and CD<sub>2</sub>O and we have no evidence for this. The possibility that CH<sub>2</sub>O resulted from the exchange of deuterium atoms of CH<sub>3</sub>OD and CHDO with H<sub>2</sub> was eliminated by decomposing MeOH and CH<sub>2</sub>O in the presence of D<sub>2</sub>. In neither case was any exchange observed.

On the basis of the above data the following mechanism is proposed.

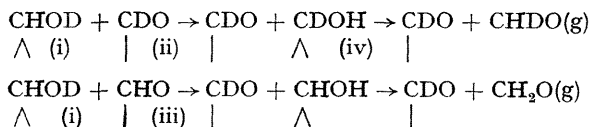
(1) The initial reaction involves the loss of two hydrogen atoms from the methyl group of methanol, followed by a surface intramolecular rearrangement leading to desorption of formaldehyde.



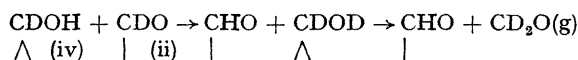
(2) The subsequent decomposition of CHDO(g) occurs by a stepwise mechanism involving the formation of one or other of two equivalent intermediate surface species, one deuteriated (ii) and the other non-deuteriated (iii).



(3) Simultaneously with CO(g) formation CH<sub>2</sub>O(g) is produced, leading finally to approximately equal concentrations of CHDO(g) and CH<sub>2</sub>O(g). This can be accounted for by the interaction of species (i) with the surface intermediates of the formaldehyde decomposition, (ii) and (iii) as suggested by the CD<sub>3</sub>OD + CH<sub>2</sub>O decomposition results.



(4) Further interactions may occur between the intermediate species; for example CD<sub>2</sub>O(g) will be a product of the reaction between (ii) and (iv).



The complexity of the mass spectra prevented observation

of small concentrations of CD<sub>2</sub>O in the presence of appreciable concentrations of CH<sub>3</sub>OD, CHDO and CH<sub>2</sub>O; the estimated maximum CD<sub>2</sub>O concentration that could have been present was *ca.* 20 × 10<sup>16</sup> molecules.

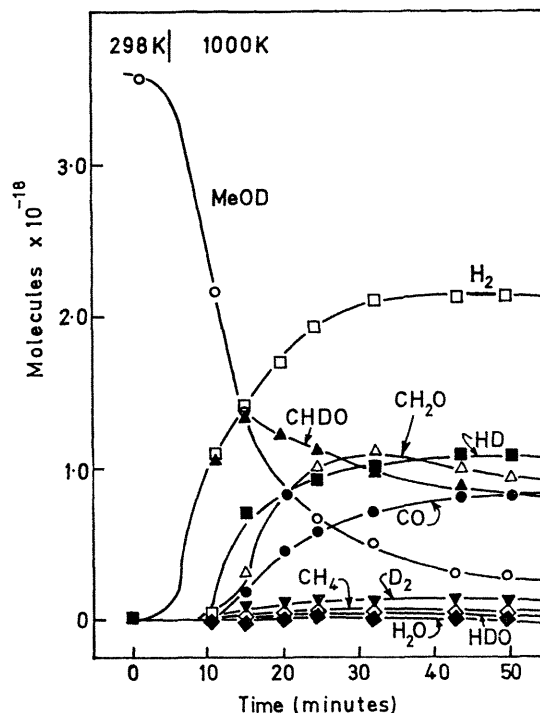


FIGURE. Analysis of the gas phase during the decomposition of CH<sub>3</sub>OD on gold at 1000 K.

(5) CH<sub>4</sub> and water were observed as minor decomposition products (Figure) *via* the breakdown of species formed subsequent to cleavage of the carbon–hydrogen bond which occurs to only a very small extent on gold (*cf.* CH<sub>3</sub>OH on Ni<sup>1</sup>). The absence of deuteriated methane, and HDO formation in excess of H<sub>2</sub>O further indicates the tendency of the oxygen–hydrogen bond to be retained during decomposition.

It may be concluded that the initial reaction involves the abstraction of two hydrogen atoms from the adsorbed CH<sub>3</sub>OD molecule, resulting in the formation of CHDO and H<sub>2</sub>. The CHDO is readsorbed on to the gold surface and either decomposes to CO and HD, or interacts further with an adsorbed intermediate formed during CH<sub>3</sub>OD decomposition leading to the formation of CH<sub>2</sub>O. The mechanism proposed suggests that approximately equal concentrations of HD, CH<sub>2</sub>O, and CHDO and twice this concentration of H<sub>2</sub> would be formed. This is in accord with the data, if we neglect the minor products CH<sub>4</sub>, H<sub>2</sub>O, HDO, and D<sub>2</sub> (Figure), and the fact that small quantities of CD<sub>2</sub>O present would not be detectable.

We are grateful to the S.R.C. for a Research Studentship (to J. G. H.)

(Received, February 19th, 1971; Com. 147.)

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