NOTES

Reactions of Methanol, Ethanol, Dimethyl and Diethyl Ethers on Titanium

Leith, Hightower and Harkins (1) report that methanol vapor reacts with titanium films at 393–423 K to form $Ti(OCH_3)_4$, the alcoholic hydrogen being absorbed by the titanium to form hydrides. By use of carbon-13 and oxygen-18 labeled methanol, it was shown that the formation of the methoxide was not accompanied by C–H or C–O bond fission. On the other hand, C–O bond fission is recorded in the selective dehydration of formic acid (2) and isopropanol (3), and C–Cl bond fission in reactions with methyl and methylene chlorides (4). In the latter reactions all of the chlorine was retained by the titanium. Below we show that reactions of alcohols and ethers at high temperatures follow the same pattern as those of alkyl chlorides in that C–O bond fission occurs with more than 90% of the oxygen being taken up by the titanium. The gaseous products are mainly hydrocarbons.

Reactions of pure dry CH_3OH, C_2H_5OH, $(CH_3)_2O$ and $(C_2H_5)_2O$ were carried out in the range 523–733 K at pressures of 1–3 kN m^{-2} in a 176 cm^3 Pyrex reaction vessel attached to a conventional high-vacuum system. By use of a sampling valve, $\sim 0.5\%$ of the reaction mixture could be withdrawn from the center of the vessel for analysis by gas chromatography with columns of either 1.7 m Porapak Q in series with 0.6 m 8% carbowax 1540 on silanized chromosorb W, or (for hydrocarbons only) 2 m 3% squalane on activated alumina. CO was determined by use of a mass spectrometer.

Titanium films were deposited with the vessel at 273 K by evaporation from an electrically heated degassed loop of 99.7% pure wire at a pressure less than 10^{-4} N m^{-2}. The films were sintered for 10 min at reaction temperature and used immediately. As shown by BET measurements with krypton at 77 K, film areas after sintering were approximately geometrical irrespective of weight in the range 10–20 mg.

With CH_3OH at 523 K, a rapid reaction occurred initially during which 25% decomposed to give mainly CH_4 and C_2H_6 in the ratio 5:2, while at 623 K 70% reacted to give the same products in the ratio 4:1. Thereafter, C_2H_6 formation virtually ceased, but formation of CH_4 continued slowly. Minor products were CO and $(CH_3)_2O$ together with traces of C_2H_4, C_3H_6 and C_3H_8. At the end of runs at the higher temperatures, the sum of the minor products was equivalent to $\sim 7\%$ of the initial CH_3OH. Water was not found in the products. During runs at all temperatures, carbon balances and analysis of used films showed that appreciable amounts of the initial CH_3OH carbon were taken up by the titanium: 25% by the end of a run at 523 K and 10% at 623 K. None of this carbon was returned to the gas phase as hydrocarbons on exposure of a used film to H_2 at the reaction temperature. There was no evidence (1) for the formation of $Ti(OCH_3)_4$. At 633 K, second runs compared with first runs on a film were about four times slower, the initial rapid stage

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was of small extent, very little C_2H_6 was formed, but formation of $(CH_3)_2O$ was increased 4-fold. Results for films pretreated with 2.4 kN m^{-2} water vapor at reaction temperature followed by 15 min evacuation were similar to those for second runs except that less $(CH_3)_2O$ was formed. Within the range 1–3 kN m^{-2}, the initial rate was independent of CH_3OH pressure. Plots of percentage of CH_3OH reacted against (time)$^{1/2}$ show (Fig. 1) that the reaction occurring after the initial rapid process obeys a parabolic kinetic law. The latter behavior is observed for a much larger part of the reaction in second and water-pretreatment runs than in first runs. Uptake of H_2 by a fresh titanium film occurred rapidly at 623 K but not at a measurable rate when a film was exposed to a 1:1 H_2:CH_3OH mixture. Runs with 1:1 and 2:1 mixtures showed that the main effects of the H_2 were to halve the extent of the rapid initial process and to increase the CH_4:C_2H_6 ratio in the products to 10:1.

Reactions of C_2H_5OH at 527–615 K were analogous to those of CH_3OH, the main products being C_2H_6 and C_4H_{10} (ratio 2:1 at 586 K) with minor amounts of CO, $(C_2H_5)_2O$, CH_4, C_2H_4, C_3H_6 and C_3H_8. The kinetic behavior was very similar to that for CH_3OH.

$(CH_3)_2O$ reacted at 673–733 K to give CH_4 as the main product. Depending on temperature, $\sim 5\%$ of the ether was con-

verted to C_2 and C_3 hydrocarbons, while carbon uptake by the titanium was equivalent to $\sim 20\%$ of the initial ether. However, in runs at 673 K with H_2–$(CH_3)_2O$ mixtures of ratio 2:1, the carbon uptake was only 2% and more CH_4 was formed. The rapid initial process observed with CH_3OH did not occur with the ether, and a parabolic kinetic law was obeyed throughout the reaction. At 586–668 K, $(C_2H_5)_2O$ gave C_2H_6 and C_2H_4 in 5:4 ratio as the main products, $\sim 5\%$ of the ether being converted to C_4H_{10} and $\sim 6\%$ to C_1 and C_3 hydrocarbons. Carbon uptake was equivalent to $\sim 20\%$ of the ether, but to only $\sim 5\%$ when a 4:3 H_2–ether mixture was used. A rapid initial reaction involving 10–20% of the ether occurred, whereafter the reaction followed a parabolic kinetic law.

It is evident from the nature of the gas phase products that C–O bond cleavage occurs with both of the alcohols and ethers, and that practically all of the oxygen is retained by the titanium. Following C–O fission in the alcohols, alkyl groups either react with OH groups or combine in pairs to give the principal saturated hydrocarbon products. Some O–H fission in the alcohols is required to account for the minor amounts of ethers formed. In reactions of ethers, the main products can be accounted for if an alkyl group reacts by hydrogen abstraction from, or by disproportion with, a second group. In all cases, the formation of the minor hydrocarbon products and the uptake of carbon by the titanium suggest that progressive degradation of alkyl groups to carbon can occur. The fact that the amount of methanol carbon taken up by the titanium is higher at 523 K than at 623 K suggests that the lower the temperature the greater is the tendency for adsorbed species to degrade to carbon rather than to react with the release of hydrocarbons. As far as the titanium is concerned, the reaction appears to be essentially one of oxidation, and the
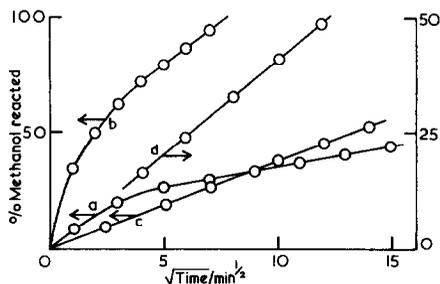

FIG. 1. Plot of percentage of methanol reacted against square root of time: (a) first run 522 K; (b) first run 621 K; (c) second run 621 K; (d) run with H_2O pretreatment 608 K.

incidence of parabolic kinetics indicates that a type of diffusion process is involved. The total amount of oxygen taken up by the titanium was equivalent to ~ 50 monolayers of O_2 molecules. We suggest therefore that in the initial stage of the reactions, or during water pretreatment, a thin oxide layer which may contain carbide is built up, and thereafter the rate is controlled by the growth of this layer involving diffusion of oxygen-containing species through or across the layer. Activation energies calculated from the temperature coefficient of k in the expression: percentage decomposition $= kt^{1/2}$ were 38 kJ mole^{-1} for CH_3OH and 15 kJ mole^{-1} for $(CH_3)_2O$. It is significant that oxidation of titanium by oxygen is known to obey a parabolic kinetic law (5).

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