CATALYTIC RESULTS FOR THE WO_3/ZrO_2 CATALYST

Dehydration of Mixed Alcohols. A kinetic study was carried out with mixtures of methanol and isobutanol at a total reaction pressure of 1.36 MPa. In these studies, the partial pressure of one alcohol was maintained constant while the partial pressure of the other alcohol was varied. This allowed for determination of reaction rates and kinetic parameters for isobutanol dehydration to form isobutene (IB) and coupling reactions to form dimethylether (DME), diisobutylether (DIBE), and methylisobutylether (MIBE) using Equations (2)-(5).

$$v_{DME} = k_1 K_M{}^2 p_M{}^2 / (1 + K_M p_M + K_B p_B)^2 \quad (2)$$

$$v_{DIBE} = k_2 K_B{}^2 p_B{}^2 / (1 + K_M p_M + K_B p_B)^2 \quad (3)$$

$$v_{IB} = k_3 K_B p_B / (1 + K_M p_M + K_B p_B)^2 \quad (4)$$

$$v_{MIBE} = k_4 K_M p_M K_B p_B / (1 + K_M p_M + K_B p_B)^2 \quad (5)$$

In these equations utilized for determining the formation rates (v_i) of the products, p_M is the partial pressure of methanol, p_B is the partial pressure of isobutanol, the k_n values are the kinetic constants, and the K_n values are the adsorption equilibrium constants.

Results obtained at reaction temperatures of 127°C and 176°C are shown in Figure 1, which represents MIBE formation rates as a function of partial pressure of each reactant while keeping the pressure of the second alcohol constant. Symbols represent experimental data at 150°C and the full lines are theoretical curves based on Langmuir-Hinshelwood kinetics as described in Nunan et al. [6]. The MIBE formation rates show maxima in the dependence on partial pressures of both alcohols at both reaction temperatures, which implies optimum regime for the MIBE synthesis by either alcohol. The kinetic and adsorption equilibrium constants were obtained by fitting Equation (5) given above.

Figure 2 shows examples of using the linear forms of the rate laws, where (a) the partial pressure of isobutanol was maintained constant at 13 kPa while varying the methanol partial pressure and (b) methanol was maintained constant at 23 kPa while varying the isobutanol partial pressure. These linear plots yield the slopes and intercepts for experiments in which pM and pB were separately varied. The ratio of the intercept to the slope in each linear plot provided $(1 + K_B p_B) / K_M$ and $(1 + K_M p_M) / K_B$, respectively. Since p_M and p_B were set as constants, K_M and K_B could be determined unambiguously.

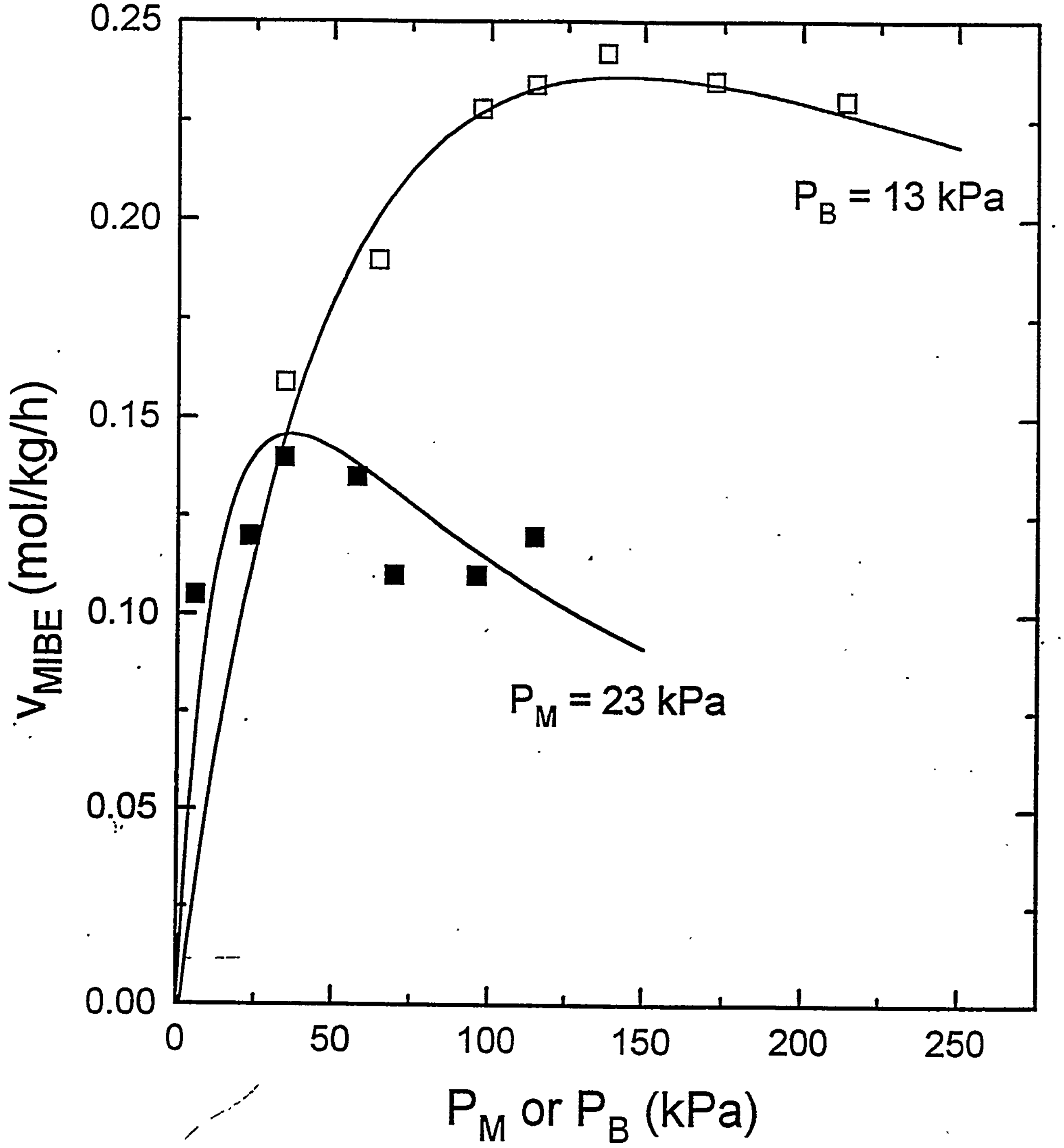

Figure 1. Rates of MIBE formation from mixtures of methanol and isobutanol as a function of partial pressure of methanol, p_M, while keeping partial pressure of isobutanol, p_B, constant at 13 kPa (□), and p_B with constant p_M at 23 kPa (■) over 1.0 g of the tungstena/zirconia (WZ) catalyst. The reaction conditions were 150°C, p_{total} =1360 kPa, and 18.7% N_2/He + alcohol feed rate of 125 mol/kg catalyst/h. Squares are experimental data and full lines are theoretical curves obtained by using Eq. (5) for the dependence of v_{MIBE} on p_M and p_B with k_4 = 3.1 mol/kg/h, K_M = 0.010 kPa^{-1}, and K_B = 0.034 kPa^{-1}.

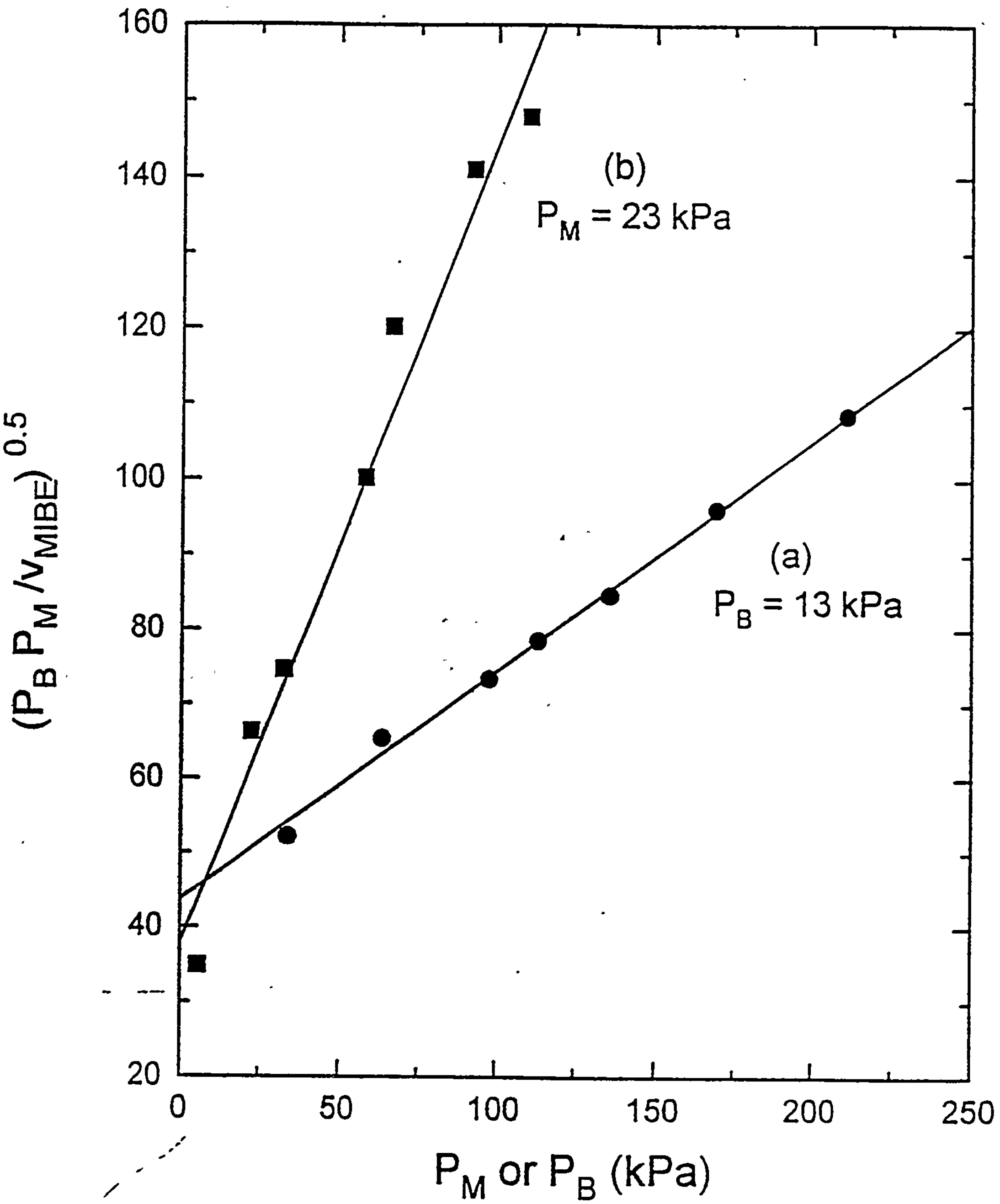

Figure 2. Langmuir-Hinshelwood linear plot for the dehydration of methanol and isobutanol to MIBE over 1.0 g tungstena/zirconia catalyst at 150°C, $p_{total} = 1360$ kPa, and 18.7% N_2/He + alcohol feed rate of 125 mol/kg catalyst/h. The slope and intercept give combinations of rate and equilibrium constants (a) $\sqrt{(K_M/(k_4K_B))} = 0.309$ and $(1 + K_bp_B)\sqrt{(k_4K_MK_B)} = 43.8$, with $p_B = 13$ kPa and varying the partial pressure of methanol p_M, and (b) $\sqrt{(K_B/(k_4K_M))} =$ 1.05 and $(1 + K_mp_M)\sqrt{(k_4K_MK_B)} = 37.95$, with $p_M = 23$ kPa and varying the partial pressure of methanol p_B. k_4 is in mol/kg catalyst/h and K_M and K_B are in kPa^{-1}.

The kinetic and adsorption equilibrium constants were $k_4 = 3.1$ mol/kg/h, $K_M = 0.010$ kPa^{-1}, and $K_B = 0.034$ kPa^{-1} at 150°C. At 127°C, theoretical curves with $k_4 = 0.93$ mol/kg/h, $K_M = 0.011$ kPa^{-1}, and $K_B = 0.039$ kPa^{-1} successfully fitted the experimental data. The ratio of K_B/K_M was 3.4 at 150°C and 3.5 at 127°C, respectively, implying that isobutanol adsorbs more strongly to the active sites on the surface than methanol. Under similar reaction conditions (127°C and 1340 kPa), Nafion-H was reported to have the following constants: $k_4 = 2.78$ mol/kg/h, $K_M = 0.0137$ kPa^{-1}, $K_B = 0.0243$ kPa^{-1}, and $K_B/K_M = 1.8$ [6]. Although the constants are of the same order of magnitude, Nafion H turned out to be approximately 2.4 times more active for MIBE production than the present tungstena/zirconia catalyst.

With the rate constant obtained at 150 °C and activation energy (discussed later in this report) for MIBE formation, k_4 at 127°C could be determined from the Arrhenius rate expression, $k_4 = A \exp(-E_a/RT)$. The k_4 value was determined to be 1.04 mol/kg/h with a pre-exponential factor of $A = 5.7 \times 10^8$. This value of k_4 is very close to that determined from the separate experiment described above. In addition, the equilibrium constants K_B and K_M could also be determined from the data for DME and IB formation by using the linearized forms of Equations (2) and (4). The resulting linear plots were shown in Figure 3, yielding $K_M = 0.015$ kPa^{-1} and $K_B = 0.037$ kPa^{-1} (and $k_4 = 2.7$ mol/kg/h). The theoretical curves with the equilibrium and kinetic constants so obtained deviated appreciably from the experimental data and did not fit the experimental data as well as those shown in Figure 1. However, correct trends were predicted, and the values of K_B and K_M were not too different from those determined from the MIBE experiment, as shown in Figure 1 with derived values of K_B and K_M of 0.034 and 0.010 kPa^{-1}, respectively.

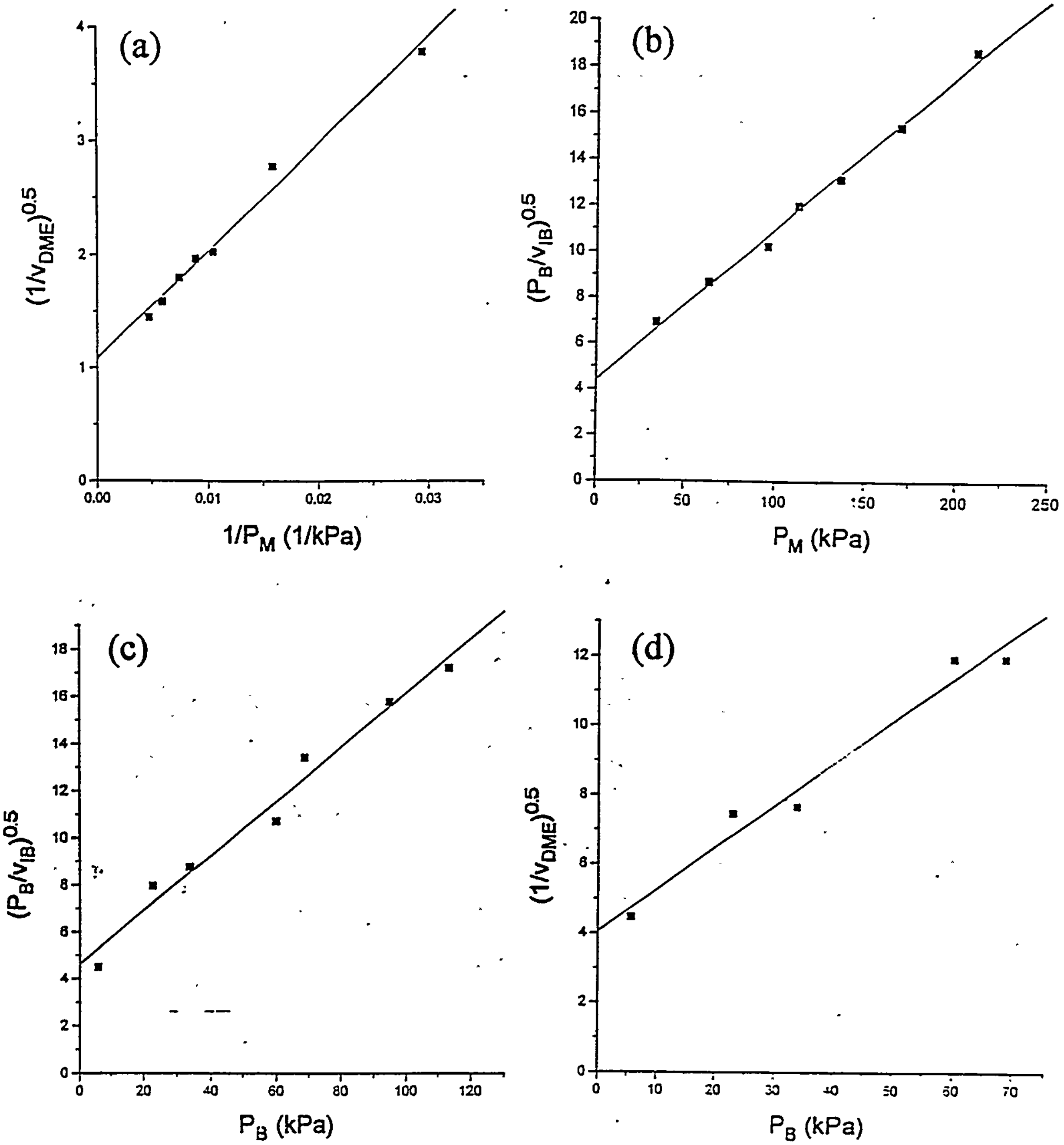

Figure 3. Langmuir-Hinshelwood linear plot for the dehydration of methanol and isobutanol to MIBE over 1.0 g tungstena/zirconia catalyst at 150°C, $p_{total} = 1360$ kPa, and 18.7% N_2/He + alcohol feed rate of 125 mol/kg catalyst/h. The slope and intercept give combinations of rate and equilibrium constants (a) $\sqrt{k_1} = 1.08$ and $(1 + K_B p_B) / \sqrt{(k_1 K_M^2)} = 94.7$ and (b) $K_M \sqrt{(k_3 K_B)} = 0.066$ and $(1 + K_b p_B) / \sqrt{(k_3 K_B)} = 4.39$ where $p_B = 13$ kPa and the partial pressure of methanol p_M was varied, and (c) $\sqrt{(K_B/k_3)} = 0.116$ and $(1 + K_m p_M) / \sqrt{(k_3 K_B)} = 4.61$ and (d) $K_B / \sqrt{(k_3 K_M p_M)} = 0.122$ and $(1 + K_m p_M) / \sqrt{(k_1 K_M p_M)} = 4.04$, where $p_M = 23$ kPa and the partial pressure of methanol p_B was varied. k is in units of mol/kg catalyst/h and K_M and K_B are in units of kPa^{-1}.

Dehydration of Individual Alcohols. Experiments were also carried out using only one of the alcohols as a reactant at 127°C and p_{total} = 1360 kPa. In methanol dehydration in the absence of isobutanol, DME was the only reaction product observed, and the formation rate was leveling off at high methanol pressures (Figure 4). For isobutanol dehydration, isobutene and isooctene were the major products. The cis- and trans-2-butenes were observed as minor products, but no diisobutylether (DIBE), which is one of the significant products over Nafion H, was detected. The rates of formation of the major products formed from isobutanol are shown in Figure 5. Using the same graphical analysis methods as previously described, the plots shown in Figure 6 were obtained. The kinetic and equilibrium constants from this analysis of the reactions of the individual alcohols were determined to be in the same order of magnitude (K_M = 0.014-0.047 kPa^{-1} and K_B = 0.0196 kPa^{-1}). Although the K_M value from MIBE synthesis with mixed alcohols was within the range of the value of K_M obtained from the methonol-only experiment, the K_M value varied depending on p_M, implying failure of the Langmuir-Hinshelwood kinetic analysis based on Equation (2). Further data analysis will be carried out to obtain an explanation and/or a better kinetic equation.

Temperature Effect on Selectivity. In order to elucidate the effect of temperature on product selectivity over the tungstena/ zirconia catalyst, the reaction temperature was varied between 127°C and 150°C while keeping the total pressure constant at 1360 kPa. The reactant ratio methanol/isobutanol = 2 was maintained. The product selectivity as a function of temperature is shown in Figure 7. At 127°C, MIBE was the dominant product, but at

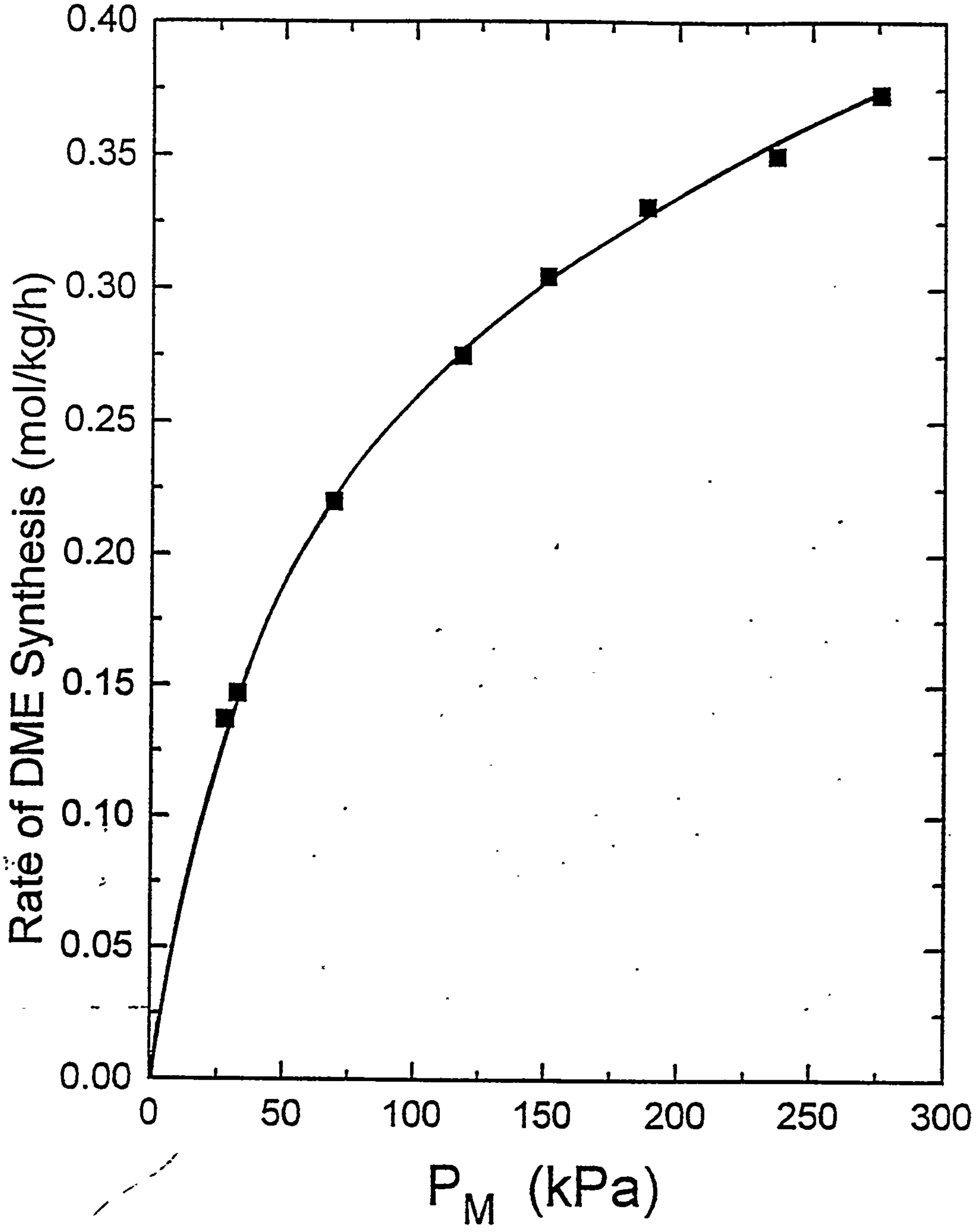

Figure 4. Effect of methanol partial pressure (p_M) on the steady state rate of formation of DME over 1.0 g tungstena/zirconia at 127°C, p_{total} = 1360 kPa, and 18.7% N_2/He + alcohol feed rate of 125 mol/kg catalyst/h.

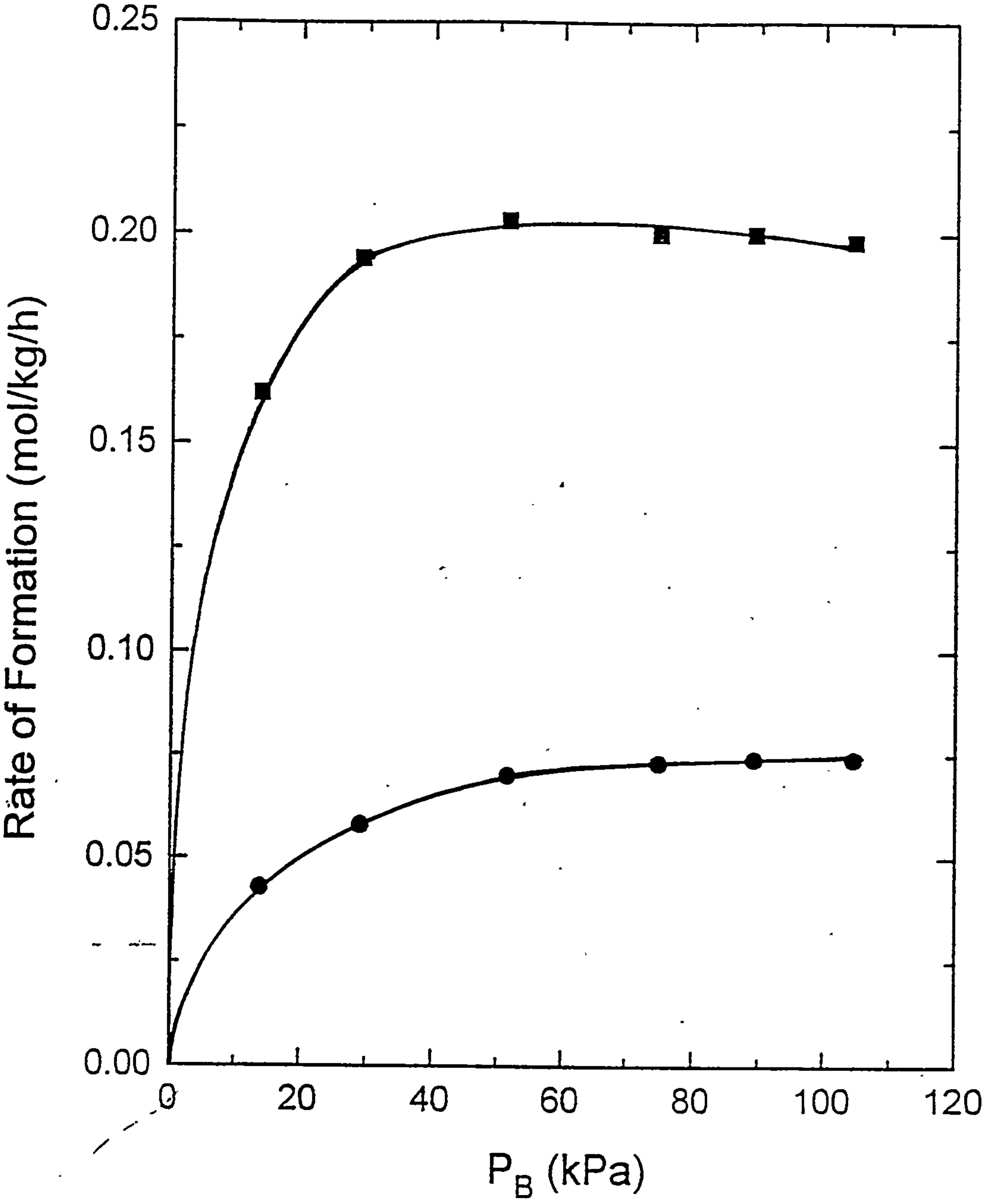

Figure 5. Effect of isobutanol partial pressure (p_B) on the steady state reaction rates for the major products, isobutene (■) and isooctene (●), over 1.0 g tungstena/zirconia at 127°C, p_{total} = 1360 kPa, and 18.7% N_2/He + alcohol feed rate of 125 mol/kg catalyst/h.

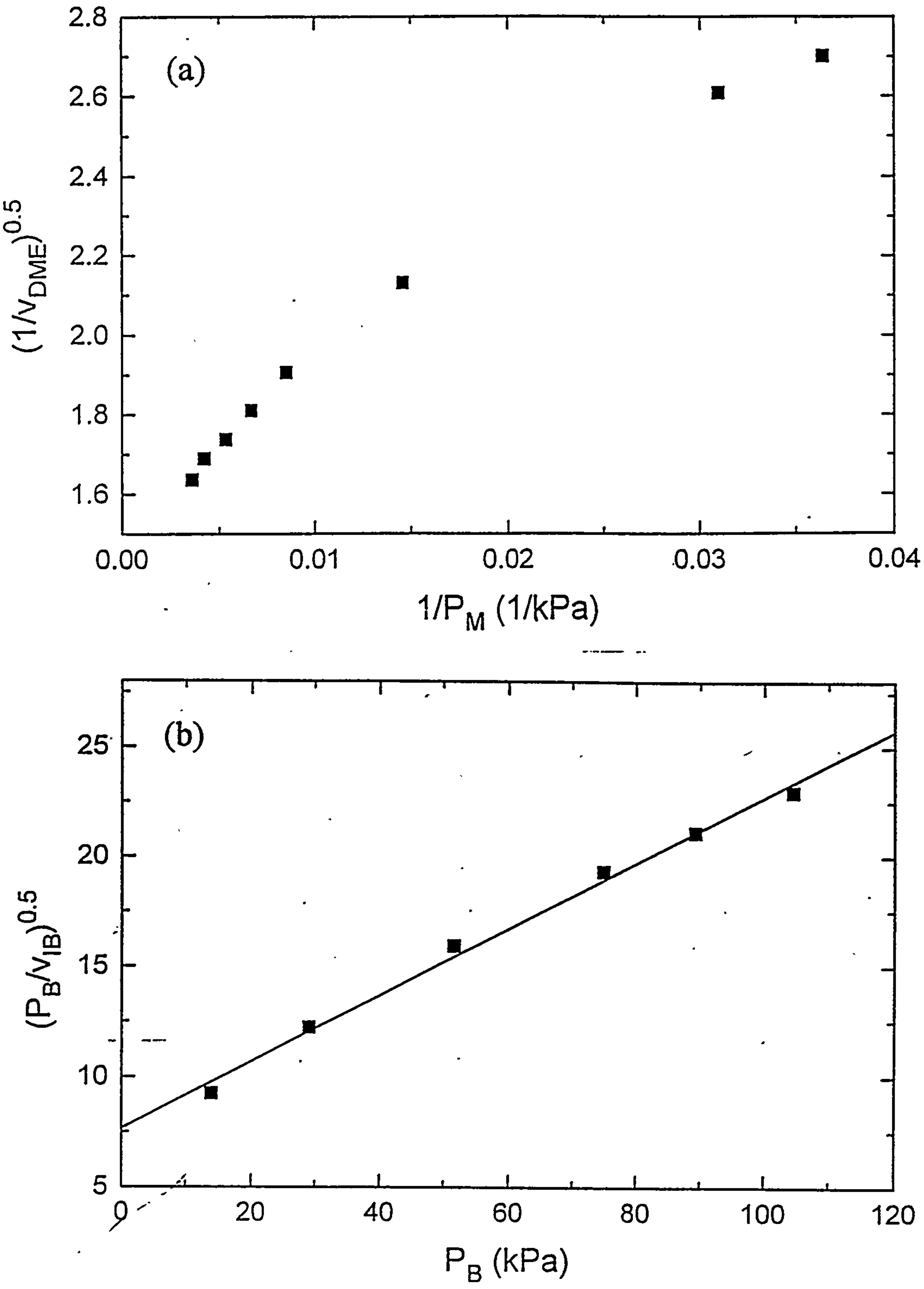

Figure 6. Langmuir-Hinshelwood linear plot for the dehydration of (a) methanol and (b) isobutanol over 1.0 g tungstena/zirconia catalyst at 127°C, $p_{total} = 1360$ kPa. The slope and intercept give combinations of rate and equilibrium constants (a) $1 / \sqrt{k_1} = 1.25$ for the two highest p_M data points and 2.06 for the two lowest p_M data points and $1 / \sqrt{k_1 K_M} = 91.3$ and 17.8, respectively, and (b) $\sqrt{(1 / (k_3 K_B))} = 7.7$ and $\sqrt{(K_B / k_3)} = 0.15$. k is in units of mol/kg catalyst/h and K_M and K_B are in kPa^{-1}.

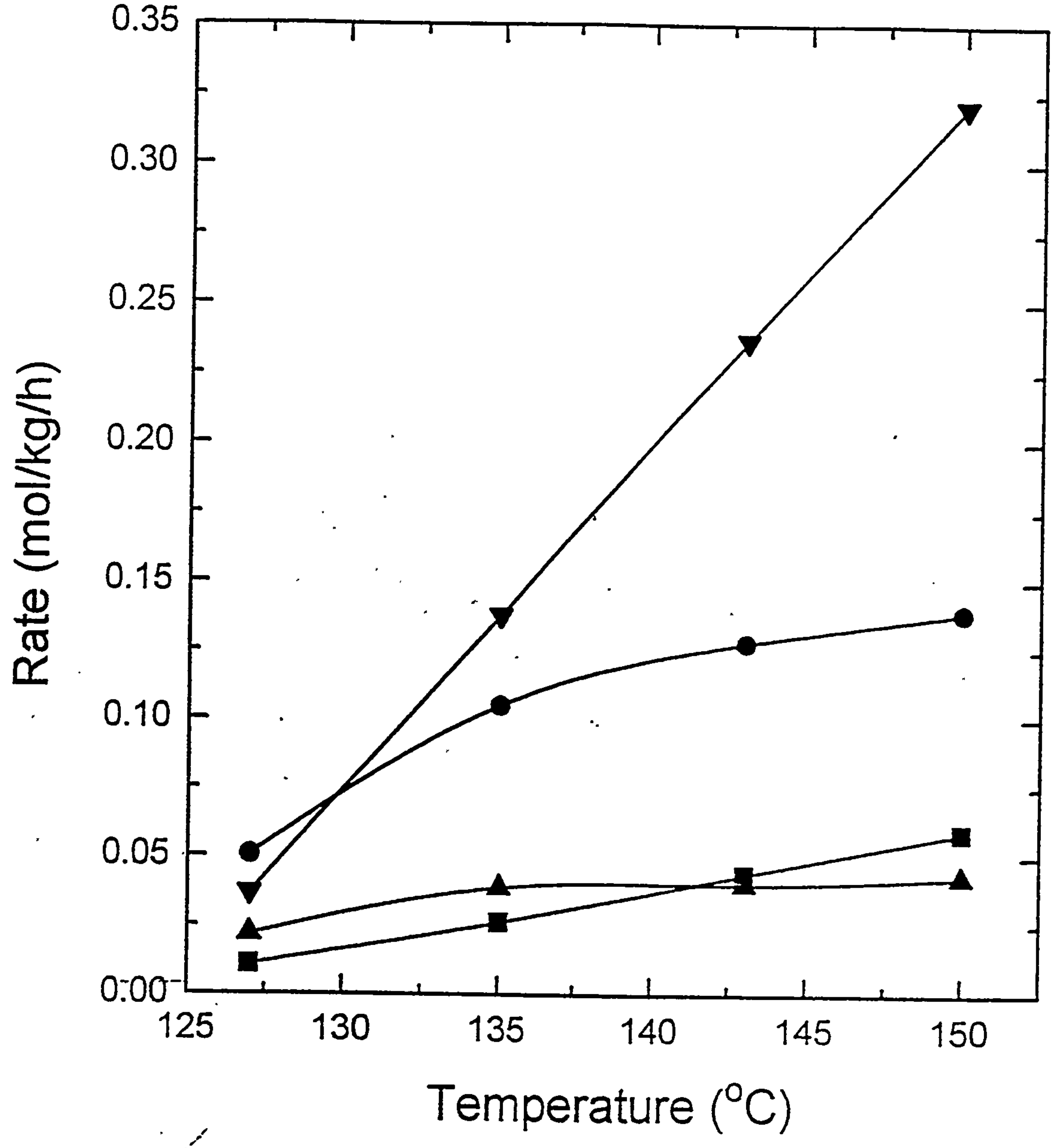

Figure 7. Effect of temperature on the steady state reaction rates of MIBE (●), butenes (▼), octene (▲), and DME (■) over 1.0 g tungstena/zirconia with methanol/isobutanol = 2/1 at p_{total} = 1360 kPa, and 18.7% N_2/He + alcohol feed rate of 125 mol/kg catalyst/h.

higher temperatures (>130°C) butenes predominated. The butenes, octenes, and DME were the next in decreasing order. Increasing the reaction temperature resulted in an increase in the formation of all products, but butenes were the dominant product at 135°C and higher temperatures. MIBE became the second most abundant product. MTBE, an isomer of MIBE, was formed in a smaller amount, typically 5% of the amount of MIBE regardless of reaction temperature. Among butenes, isobutene was the major product, while linear butenes formed between 15 and 25% of the amount of isobutene. Thus, the higher the reaction rate, the larger the quantity of linear butenes that were formed. Among the octenes, 2,5-dimethylhexene was predominant over the entire temperature range, with increasing selectivity to 2,2,4-trimethylpentene as temperature increased.

The apparent activation energy for the formation of individual products was determined from Arrhenius plots, as shown in Figure 8. Apparent activation energies were as follows: 113 ± 8 kJ/mol for DME, 67 ± 17 kJ/mol for MIBE, 121 ± 29 kJ/mol for isobutene, and 38 ± 17 kJ/mol for isooctene. In the case of gel-type Nafion H at 1344 kPa, the values determined were 84.2-87.5 kJ/mol for DME, 84.3 kJ/mol for MIBE, 144.6 kJ/mol for butenes + octenes [8]. In comparison, with a porous Nafion-H MS catalyst at 7600 kPa, the obtained activation energies were 79 kJ/mol for DME, 61 kJ/mol for MIBE, and 227 kJ/mol for isobutene [14]. The activation energies for ether formation are thus lower than the activation energies for olefin formation on both WZ and Nafion-H catalysts.

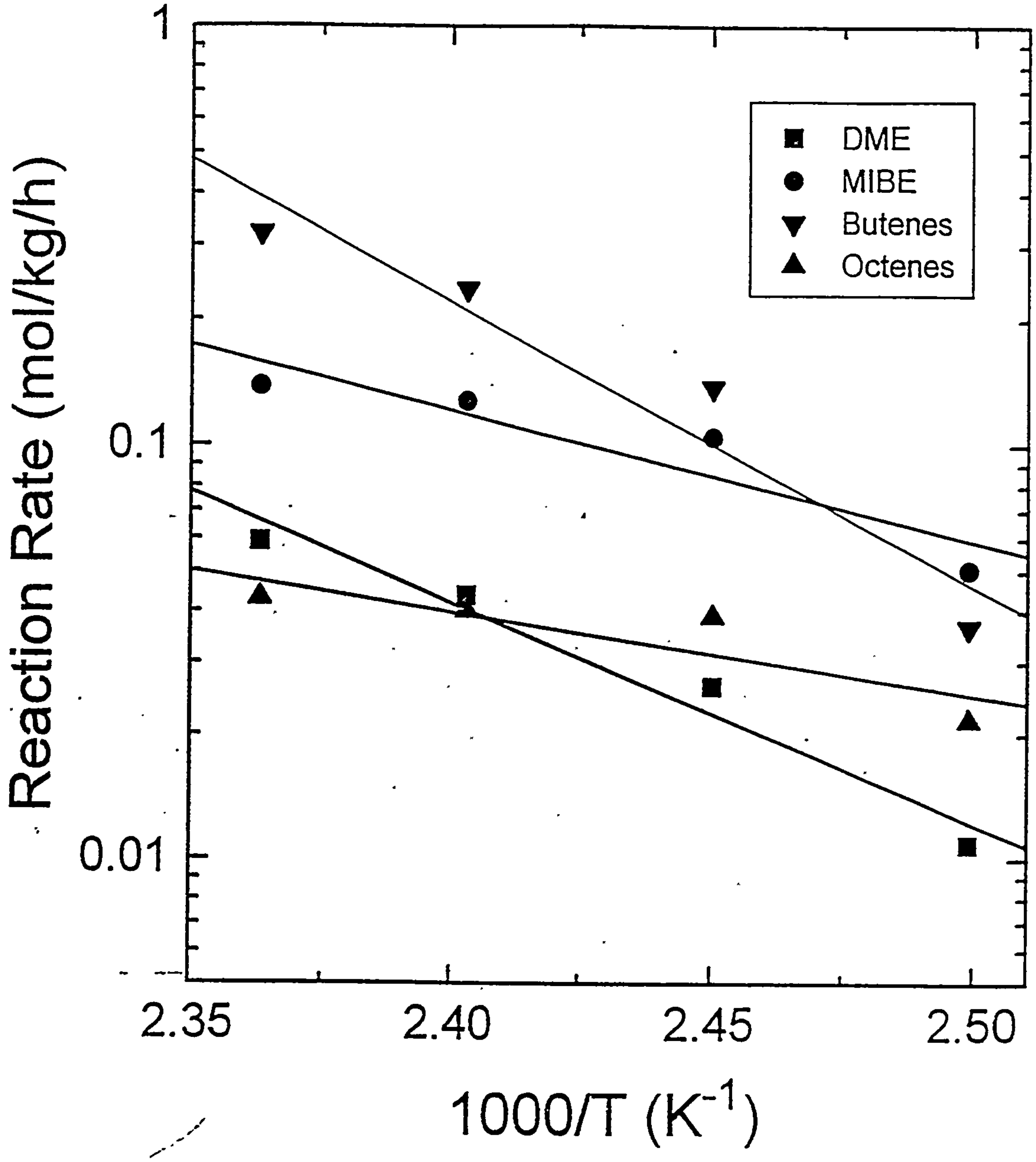

Figure 8. Arrhenius plots of the formation rates of the major products MIBE (●), butenes (▼), octenes (▲), and DME (■) formed over the tungstena/zirconia catalyst with methanol/isobutanol = 2/1 at p_{total} = 1360 kPa, and 18.7% N_2/He + alcohol feed rate of 125 mol/kg catalyst/h.