Reactions of Methane with Unsaturated Hydrocarbons in the Presence of Nickel Catalysts

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Methane, when used to activate supported nickel catalysts, reacts at *ca.* 300 °C with benzene, cyclopentene, methylenecyclopentane, and simple alkenes to give modest but definite amounts of higher hydrocarbons.

Methane, a raw-material of great potential synthetic importance, is still used mainly as a fuel; only small amounts are consumed in the water gas processes.[1] However, methane reacts with alkanes under oxidative conditions[2] and in the presence of superacids[3] or Ziegler–Natta catalysts.[4] On aluminosilicates[5] and with various additives (*e.g.*, dinitrogen oxide),[6] methane forms C_6 to C_{12} aromatic hydrocarbons. Alkanes are dimerized at 25 °C on a silver-loaded zeolite by u.v. light.[7] Electron beam irradiation of a CH_4/CO_2 mixture results in the formation of hydrocarbons and hydrogen.[8] Furthermore, discharge and plasma methods[9] as well as oxidative pyrolysis[10] convert methane into hydrocarbons, *e.g.*, C_2H_2, C_2H_4. The addition of CH_4 to aldehydes followed by water elimination gives alkenes.[11] H/D exchange,[12] metal

Table 1. Gibbs free energy changes for some gas phase reactions.[a]

	Reaction	ΔG° (react.) kcal/mol[b] 300 K	500 K	700 K
1	$2CH_4 \rightarrow C_2H_6 + H_2$	+16.43	+16.86	+17.02
2	$C_3H_8 + CH_4 \rightarrow$ i-$C_4H_{10} + H_2$	+12.78	+14.01	+14.88
3	$C_6H_6 + CH_4 \rightarrow C_6H_5CH_3 + H_2$	+10.32	+10.31	+9.96
4	C_3H_6[d] + $CH_4 \rightarrow$ i-C_4H_{10}[c]	−7.77	−0.21	+7.21
5	c-C_5H_8[e] + $CH_4 \rightarrow$ c-$C_5H_9CH_3$[f]	−5.73	+0.74	+7.03
6	c-$C_5H_9CH_3$[f] $\rightarrow C_6H_6 + 3H_2$	+22.31	+6.24	−10.57
7	4c-C_5H_8[e] + $CH_4 \rightarrow C_6H_6$ + 3c-C_5H_{10}[g]	−34.99	−25.63	−16.50

[a] Ideal gas values at 1 atm calculated from data in ref. 16. [b] 1 kcal = 4.18 kJ. [c] Isobutane. [d] Propene. [e] Cyclopentene. [f] Methylcyclopentane. [g] Cyclopentane.

atom insertion,[13] and activation of methane and other saturated hydrocarbons by homogeneous catalysis[14] has been demonstrated in a number of intriguing studies.

We now report experimental observations that methane reacts with unsaturated compounds under heterogeneous gas phase conditions. Catalytic processes, such as the reaction of 2-methyladamantane with hydrogen to give adamantane and methane quantitatively at 220 °C on an active Ni/Al_2O_3 catalyst,[15] form equilibria and the reverse reaction should also be possible. However, thermodynamic considerations[16] show the reaction of methane with itself or its addition to unstrained saturated hydrocarbons to be unfavourable under any reasonable reaction conditions [see Table 1, reactions (1) and (2)].

Nevertheless, up to 7% toluene was formed by reaction of methane with benzene at 300 °C on a Ni/SiO_2 catalyst at atmospheric pressure [see Table 1, reaction (3)]. This is the reverse of the technical benzene production by hydrogenolysis of toluene.[17] In the control experiment using argon as the carrier gas instead of methane, only benzene was recovered.

The addition of methane to an olefinic C=C double bond (the formal equivalent of hydrogenation) is exothermic at lower temperatures [see Table 1, reactions (4) and (5)]. The reaction of methane with cyclopentene at 310 °C and atmospheric pressure (with a 20% Ni on sodalite catalyst) gave benzene in 33% yield and smaller amounts of toluene (9%) and cyclopentane (13%). Control runs with nitrogen carrier gas gave only 5% benzene, demonstrating the participation of methane. Higher pressure (up to 10 atm) experiments which allowed greater surface occupation gave mostly cyclopentane and very little benzene.

Methylcyclopentane [see Table 1, reaction (5)] is a possible intermediate. Subsequent ring enlargement and dehydrogenation [dehydroisomerization, Table 1, reaction (6)] are well known heterogeneous catalytic processes.[18] The overall process is particularly favourable thermodynamically [Table 1, reaction (7)], but the amount of cyclopentane in the product never corresponded to this stoicheiometry. Products are also formed by fragmentation of cyclopentene and recombination of the fragments on the catalyst surface.

To determine whether methane is incorporated at all, experiments with $^{13}CH_4$ were performed. Our general procedures are important. The catalyst was prepared by the incipient wetness technique[19] using a nickel nitrate solution to impregnate the carrier, *e.g.*, silica. After drying, the catalyst is normally activated by hydrogen reduction at higher temperatures, but we used methane instead of hydrogen for this purpose. This undoubtedly leads to a nickel surface associated with carbonaceous fragments. In the first set of experiments, the nickel salt was first reduced to the metal using ordinary methane ($^{12}CH_4$) in a continuous flow system. When the subsequent reaction with cyclopentene was carried out using $^{13}CH_4$ as the carrier gas, *no excess ^{13}C labelled compounds were found in the product mixtures.*

When both the reduction of the catalyst and the subsequent reaction with cyclopentene were carried out using $^{13}CH_4$, the isotope was incorporated but only to a modest extent. The products were only singly labelled: 7% of the benzene and 10% of the toluene contained one ^{13}C by mass spectrometric analysis. These results support the general conclusions reached by Tanaka *et al.*[20] in experiments with $^{13}CH_4$ on Co/Al_2O_3 catalysts. In our case, active carbonaceous species, ($^{13}CH_n$), formed by reaction of methane with the nickel salt during the catalyst reduction step, are evidently responsible for the incorporation of the label into the products, *e.g.*, by carbene-like addition to the double bond. However, other reaction mechanisms leading to benzene and toluene must also be utilized, since the percentages of ^{13}C in these products were rather small.

The reaction of methane with methylenecyclopentane gives a yield of toluene up to 23% at 300 °C, 1 atm. The reaction of methane with the alkene must precede aromatization (*e.g.*, the possible conversion of methylenecyclopentane into benzene), as benzene gives much less toluene under the same conditions (see above).

Further investigations showed that ethylene, propene, and the butenes react in the presence of methane and methane-reduced nickel catalysts to form complex mixtures of hydrocarbons. The reaction of propene, which was studied most extensively,[21] is representative. A methane/propene gas mixture (containing 6% propene) was passed over 7.5% Ni on silica at 330 °C, 10 atm. The resulting product, composed of 53% C_1,C_2, 26% C_3H_8, 8.5% C_4H_{10}, and 13% C_5,C_6 hydrocarbons, indicated methane consumption. In the control experiment using nitrogen instead of CH_4, the product composition was different: 40.5% C_1,C_2, 42% C_3H_8, 8% C_4H_{10}, and 9.5% C_5,C_6 hydrocarbons. The presence of methane resulted in slightly larger amounts of hydrocarbons having more than three C-atoms, *e.g.*, C_4H_{10} and C_5,C_6 hydrocarbons.

While yields and product distributions are still far from those needed for commercial application, methane does react with unsaturated compounds. The reactions are not simple. Methane apparently forms active CH_n–nickel species during reduction of the catalyst, and these combine with unsaturated substituents. Other hydrocarbons also form carbonaceous fragments on the catalytic surface, and give rise to similar products. The initial products on the catalyst surface are subject to isomerization, fragmentation, and further reactions.[22] When an inert carrier gas is employed, some of the carbonaceous species are removed from the surface, and lower yields of higher hydrocarbon products result.

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