Homologation of Olefins on an Iron Catalyst in the Absence of Carbon Monoxide

Richard A. Strehlow and Emily C. Douglas

Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee 37830, U.S.A.

Homologation of olefins occurs in competition with hydrogenation catalysed by iron in the presence only of hydrogen.

We have observed that homologation of olefins is catalysed by iron. Olefins have been reported to be transformed to higher molecular weight olefins in the presence of a molybdenum–alumina catalyst[1] and of nickel.[2] Alkanes homologate on tungsten films[3] (through assumed olefin intermediates) but we have found no previous report of this reaction being catalysed by iron. Pentane produces benzene on Rh and Rh–Cu alloy films[4] and on Pd, Rh, and W[3]; this process may indicate homologation followed by dehydrocylization.

Homologation reactions (apparently *via* methylidene insertion[5]) have been reported for some co-ordination complexes and mononuclear compounds of silicon and may be related to heterogeneously catalysed Fischer–Tropsch syntheses.[6] Two reports have been found of homologation by methylidene insertion in iron complexes.[7,8] Supported iron clusters have been reported to be active Fischer–Tropsch catalysts.[9–11] The fact that similar insertion reactions occur on solid iron catalysts (as observed here), an iron cluster catalyst, and co-ordination complexes of iron and other metals implies that a common mechanism for insertion may exist.

In this work we used a plug flow reactor containing a commercially available iron oxide catalyst. The catalyst was an ICI #35-4 fused magnetite catalyst with additions and nominal concentrations of K_2O (0.8%), CaO (2.0%), MgO (0.3%), Al_2O_3 (2.5%), SiO_2 (0.4%), and traces of other oxides. The catalyst was crushed and sieved to a −80 +100 mesh size. *Ca.* 3.0 g of catalyst was reduced in a 1/4 in stainless steel tube reactor and analyses of products were made using an on-line mass spectrometer. After catalytic reduction with hydrogen, various olefins were injected into the hydrogen stream (olefin: H_2 = *ca.* 1) and allowed to flow through the reactor.

Hydrogenation of the injected olefins competed with homologation to form higher olefins. Under the conditions used any higher molecular weight olefins would be expected to be reduced to alkanes; butane was obtained from but-1-ene as were the homologated, reduced products (pentane, hexane, heptane, octane, *etc.*). At ratios of olefin to hydrogen appreciably greater than unity, various aromatic compounds were observed (*cf.* the reaction on Rh[4]). The extent of homologation relative to hydrogenation varied with the hydrogen partial pressures, space velocity, and temperature. Figure 1 shows the homologation of but-1-ene to pentene as a function of space velocity at two temperatures. The homologation was measured as the ratio of pentane to butane formed in the competing reactions. The total yield of homologated products under some conditions was as much as 7 or 8% of the injected quantity of but-1-ene. The increase in extent of homologation with space velocity implies the existence of a mass transfer effect resulting in a diminished olefin: hydrogen ratio in the catalyst pores. We take these results to mean that homologation occurs at a rate comparable to that of hydrogenation and perhaps higher. The temperature variation of homologation indicated an apparent energy of activation of *ca.* 10 kcal/mol (40 kJ/mol) greater than that for hydrogenation.

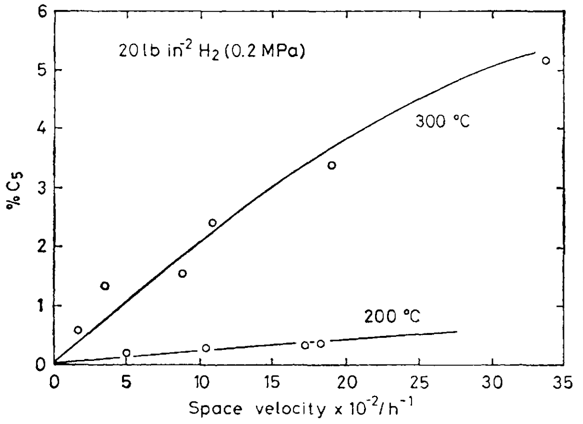

Figure 1. Extent of homologation of but-1-ene to pentene as a function of space velocity.

We believe the error in any of the data presented in Table 1 is no more than 10% of the value shown. Range switches on the amplifier were checked with a voltmeter and found to be accurate to within 1%. Adjustment was made for ionization efficiency of the parent peak of the mass spectrum which was used as the measured quantity. The parent peaks at masses of 58, 72, and 86 u were associated with residual gas peaks in the mass spectrometer, which did not exceed 20% of the measured value and were allowed for in the calculation.

The occurrence of homologation by more than one carbon atom is indicated by experiments in which the amount of two-carbon-atom chain lengthening is compared with chain lengthening by one carbon atom for different isomers of butene. Table 1 shows the yield of butene homologated with one carbon atom for three isomers and the relative yield of homologated product showing two-carbon-atom addition. In both cases the product was an alkane or was reduced to the alkane and detected as such.

The single-carbon-atom addition varies with the state of catalyst carburization, with carburized iron being noticeably less effective, but we believe the differences shown here to be representative of reactivity differences between the isomers and not to reflect progressive carburization of the catalyst. Since the single homologation occurs in competition with hydrogenation, the relative yields of single-carbon-atom homologation may reflect the differences in reactivity of a common intermediate for homologation and hydrogenation. The doubly homologated species as a fraction of the singly homologated product, shown in the final column of Table 1 shows that for *trans*-but-2-ene a larger relative amount of two-carbon-

Table 1[a]

Injected compound	Ratio $C_5H_{12}:C_4H_{10}$[b]	Ratio $C_6H_{14}:C_5H_{12}$[c]
$Me_2C{=}CH_2$	0.025	0.078
$Me(H)_2CC(H){=}CH_2$	0.014	0.057
trans-$Me(H)C{=}C(H)Me$	0.0069	0.13

[a] Gas hourly space velocity = 340 h^{-1}; 300 °C, H_2 at 35 lb in^{-2} (0.25 MPa); olefin: $H_2 \geqslant 1:2$ at iron. [b] One-carbon-atom lengthening. [c] Two-carbon-atom lengthening.

atom chain lengthening occurs than for the other two isomers. This result indicates that *trans*-but-2-ene can homologate with the addition of a two-carbon-atom group.

Although no other data have been found bearing on the intermediates of the heterogeneously catalysed homologation, we may turn to some of the speculations advanced for coordination compounds. Sumner *et al.*[8] postulated a di-iron five-membered ring in an ethylene insertion into a methylidene-iron bond, which then rearranges with hydrogen transfer and elimination as propylene. Alkylidene ligands[12] in tantalum complexes can form from olefins with incidental formation of homologated olefin. The present work supports the assumption that chain lengthening reactions are rapid and also shows that the competing hydrogenation of olefins to form alkanes can be minimized by control of the hydrogen pressure. The observed occurrence of homologation by two carbon atoms appears to add support for the existence of a metallocyclobutane intermediate as described by O'Donohoe *et al.*[3,13] and Hughes *et al.*[11]

In conclusion, we have found that olefins homologate on iron catalysts in competition with hydrogenation. Since the homologation reaction occurs to an enhanced extent at lower contact times, it appears to be a fast reaction compared with hydrogenation and may share common intermediates with the Fischer–Tropsch synthesis.

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