

Homologation of n-Alkanes on Tungsten Films. A Novel, Highly Selective Reaction of Intermediate Carbenes

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Summary The n-alkanes ($\geq C_5$) undergo a novel remarkably selective reaction in high yield whereby they are singly and multiply homologated to the higher n-paraffins during hydrogenolysis on tungsten films; the reaction, which also occurs on several other metal catalysts but there affords aromatic products at the higher temperatures employed, is discussed in terms of intermediate α -olefins and surface methylenes adding to each other in a highly selective fashion giving metallocyclobutanes, which in turn are hydrogenated to the homologous paraffin, or isomerize to new α -olefins with repetitive chain growth.

ALTHOUGH the very extensive and immediate initial degradation of paraffins to methane in excess of hydrogen

on several metal catalysts is well known,¹ little attention has been given to the thermodynamically feasible and mechanistically alternative process of simultaneous homologation. Hitherto only trace amounts of propane in hydrogenolysis of ethane have been detected,² the first significant homologation reaction being the recently reported³ formation of high yields of benzene from n-pentane on Rh-Cu alloy films. We have now found that at low hydrogen pressures, even at 423 K, on tungsten films high yields of the first homologue of the reactant are obtained in a very selective fashion during methanation of n-alkanes (Table). The yields are very sensitive to chain length, rising rapidly with the CH_2/CH_3 ratio in the n-alkane and tending to a limit at C_7 to C_9 . Furthermore the corresponding isoalkanes are at least an order of

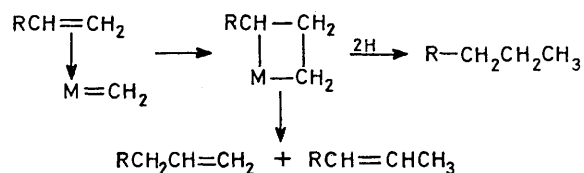
TABLE. Initial product distributions (wt %) of the reactions of alkanes on some metal films^a

Hydrocarbon	Metal ^b	H ₂ /Hc	T/K	C ₁ +C ₂	C ₃	iC ₄	nC ₄	iC ₅	nC ₅	cC ₅	nC ₆	Other products	Total rate (% min ⁻¹)
n-Pentane	W	5:1	489	48.2	19.5	0.6	24.0	2.7	—	tr.	5.0	Bn(tr.), nC ₇ (4.2)	0.33
			533	55.1	13.2	0.9	15.3	2.1	—	0.6	8.6	nC ₇ (14.7)	0.34
n-Hexane	"	2:1	485	29.3	14.7	—	16.4	—	24.1	0.8	—	nC ₇ (34.7), nC ₈ (7.5)	0.20
			539	22.1	8.5	—	9.6	—	16.1	1.5	—	nC ₈ (23.2), nC ₉ (4.9)	0.082
n-Heptane	"	2:1	513	20.7	7.3	—	8.5	—	13.4	—	22.0	MCP (1.9), 2MH (0.9)	0.11
2-Methyl-pentane	"	2:1	495	29.6	19.4	11.1	—	24.1	13.0	—	—	MCP (5.7), 2MH (1.2)	0.090
n-Pentane	Pd	10:1	631	11.2	13.3	—	11.9	3.5	—	36.4	—	CPE, CPD (10.4), Bn (13.3)	0.140
n-Pentane	Rh	7:1	573	82.6	2.5	—	3.3	—	—	—	—	Bn (11.6)	0.48

^a Hc = hydrocarbon; MCP = methylcyclopentane; Bn = benzene; 2MH = 2-methylhexane; CPD = cyclopentadiene; CPE = cyclopentene; tr = trace. ^b Evaporated *in vacuo* (10^{-5} — 10^{-6} Torr); W unsintered, Pd and Rh sintered.

magnitude less efficient in this new reaction, and cyclopentane or neopentane give no detectable trace of homologous products. On Pd or sintered Rh and at higher temperature on W (Table) chain growth is followed by rapid 1,6-cyclization and aromatization. The yields for the homologation reaction as tested with n-pentane are also sensitive to hydrogen pressure, being optimum at a ratio of 4:1 for $H_2:C_5H_{12}$. Multiple initial homologation is also observed with the higher n-alkanes.

This novel reaction on W is remarkable in its sensitivity to chain size and shape of paraffin and is equally remarkable in its selectivity in that chain branching is not observed. We believe that both of these features arise from two mechanistic requirements, namely a high flux of linear bonded surface methylenes, and a reasonable concentration of migrating α -olefins, the former being formed on degradative sites, and the latter on hydrogenation-dehydrogenation sites, either inherently present or developed in the metal surfaces as a result of partial carbiding. The mechanism is depicted in the Scheme where the carbene (CH_2) adds to



SCHEME

the C-1 carbon atom of the α -olefin exclusively, either because of steric crowding or by virtue of an electronic factor. In this respect the mechanism is very similar to

that of olefin metathesis and the present selectivity has a striking parallel to the selectivities noted for degenerate metathesis of alk-1-enes.⁴ The intermediate metallocyclobutane is then hydrogenated to the next higher paraffin or isomerizes to a new α -olefin which in turn may repeat the process of methylene addition. The isomerization to α -olefins may proceed *via* π -allyl intermediates as previously shown by Ephritikhine, Green, and MacKenzie.⁵ The absence of chain branching in homologation and lack of formation of higher products from cyclopentane is evidence that internal olefins cannot add to methylene in this fashion, because the co-ordination vacancy for the incoming olefin is sterically inaccessible to it. This explanation has a precedent in the observation of Wilkinson *et al.*⁶ that homogeneous organometallic catalysts which are highly effective for hydrogenation of alk-1-enes are sometimes practically inert for internal alkenes and cyclohexene. This selectivity also argues against other possible types of mechanism, *e.g.* carbene-carbene recombination.

The same homologation reaction proceeds on several other metals as well, *e.g.* Rh and Pd, but the mechanism here is obscured by the rapid aromatization ($\geq C_8$ chains) at higher temperatures. However the observation of significant amounts of cyclopentene and cyclopentadiene from n-pentane on Pd and the known character of this metal in exchange reactions at lower temperatures⁷ clearly support the conclusion that α -olefins are formed and migrate over the surfaces. That neopentane does not form even a trace of neohexane in spite of many experimental attempts is also evidence that α -olefins are essential intermediates and that homologation is not due simply to recombination of adsorbed fragments.

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