Conversion of Cycloheptatriene into Benzene on a Re_2O_7–Al_2O_3 Dismutation Catalyst. Formation and Reactivity of Adsorbed Methylenes

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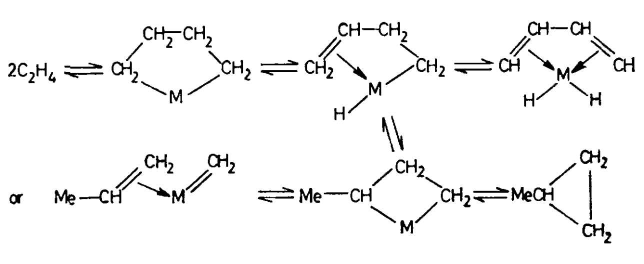
Summary Cycloheptatriene reacts readily in the presence of ethylene at >403 K on Re_2O_7–Al_2O_3 to give mainly benzene and a mixture of C_1 to C_4 products; the reaction provides good evidence for the participation of metallocycles and adsorbed methylenes in conversions of ethylene at these temperatures on dismutation catalysts.

THE observation by Banks and Bailey[1] that significant amounts of cyclopropane and methylcyclopropane are obtained in the initial products of ethylene conversion at 423 K and *ca.* 32 atm. on $Mo(CO)_6$–Al_2O_3 suggests that adsorbed carbenes may well be important intermediates in metathetic reactions of alkenes. This mechanistic implication has largely been ignored since the result seemed unique, but recently a multi-step mechanism, rather than a concerted one,[2] has been proposed[3] involving metallocycles which presumably rearrange *via* carbene complexes.[4] Information on the reactivity of simple carbenes on heterogeneous metathesis catalysts is however still very sparse.[5]

A recent report[6] showed that 1,2,3,4,5,6-hexamethylcycloheptatriene is catalytically converted into hexamethylbenzene and methylene by $[Rh(CO)_2Cl]_2$ at 393 K, but the pentamethylated homologue is inert under the same conditions. If cycloheptatriene (CHT) itself could be converted, presumably *via* intermediate norcaradiene,[6] into benzene and methylene on metathesis catalysts, not only would a special capacity for carbene formation be indicated, but an opportunity also afforded of studying the reactivity of methylene in the presence of ethylene.

Experiments were carried out in a static reactor (7×10^{-5} m^3) coupled by a gas sampling valve to a g.l.c. unit. The catalyst (0·2 g) consisting of 10% wt Re_2O_7 was outgassed at 773 K for 18 h, cooled to 273 K, CHT (10 kN m^{-2}) added and the temperature raised to (15 min) and maintained at 473 K. In additional experiments ethylene (4 kN m^{-2}) was either the sole reactant or was mixed with CHT, benzene or cyclohexa-1,4-diene (10 kN m^{-2} of each). The same procedure was used for comparative purposes since it was noted that adsorption of ethylene at 273 K prior to heating markedly enhanced its conversion at higher temperatures. Reaction of CHT commenced at 403 K giving the following initial gaseous products, ethylene (44%), propene (37%) and buta-1,3-diene (19%), and went rapidly to completion at 473 K. Methane became an important product amounting to 20% of all the methylene formed, and buta-1,3-diene hydrogenated to butenes.



The total gas yield corresponded to an 80% conversion of CHT into methylene and benzene, which was the only liquid product detected. The remaining CHT condensed to high molecular weight deposits which obviously generated the surface hydrogen required for methylene hydrogenation. The major additional feature with a mixture of CHT and ethylene was formation of cyclopropane (initially 18% of the total C_3 and C_4 products) whose yield increased little at 473 K and gradually decreased with time. There was an order-of-magnitude decrease in the yield of methane, a three-fold increase in the rate of formation of propene, and twice the initial yield of buta-1,3-diene. The catalytic activities for the conversion of CHT were in the order, $Re_2O_7 > MoO_3 > WO_3$, the same as that for propene dismutation. Ethylene by itself was slowly converted into propene at 473 K but in the presence of benzene gave both propene and buta-1,3-diene. Ethylene also reacted when mixed with cyclohexa-1,4-diene, a good hydrogen donor, but gave substantial hydrogenation of both C_2 and C_3 alkenes, no initial C_4 products, and evolution of methane. Cyclohexa-1,4-diene by itself gave no C_1 to C_4 products so formation of methane is again indicative of hydrogenation of methylene obtained in this case from ethylene.

These results support the view that metallocycles and adsorbed methylene are involved in conversion of ethylene into higher alkenes on metathesis catalysts, the trapping of methylenes by excess ethylene being preferred to hydrogenation. Clearly ethylene can be directly converted *via* a metallocyclobutane into cyclopropane and propene;[7] the former may or may not be detected depending upon conditions because of its rapid isomerization. Formation of buta-1,3-diene in the presence of a desorbing agent is also interesting since in a separate experiment but-1-ene isomerized and dismutated but did not dehydrogenate when mixed with excess benzene at > 473 K. The most reasonable explanation is that metallocycles are formed and ultimately yield diene *via* adsorbed but-1-en-4-yl. Conversion of CHT *via* norcaradiene into benzene is also an example of carbene elimination *via* decomposition of an intermediate metallocyclobutane.

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