For instance, benzene is obtained from toluene at a 90% yield. Previously it was thought that this is a bimolecular process:

$$C_6H_5CH_3 + H_2 = C_6H_6 + CH_4$$

However, studies at the Organic Chemistry Institute of the USSR Academy of Sciences have shown that for a wide range of pressures (up to 1350 atm) this is actually a complex radical-chain mechanism including the following steps:

$$C_6H_5CH_3 = C_6H_5CH_2 + H$$
 (a

$$H + C_6 H_5 CH_3 = C_6 H_6 + CH_3$$
 (b)

$$CH_3 + H_2 = CH_4 + H$$
 (c)

Reaction (a) -the rupture of the weakest bond in toluene- is the source of atomic hydrogen which interacts with a second toluene molecule in reaction (b) forming a new radical which sustains the chain mechanism in reaction (c). Most intersting is reaction (b) in which a hydrogen atom extracts the CH₂ radical from toluene.

A mechanism including an analogous step was proposed for the homogeneous destructive hydrogenation of other alkylbenzenes. In accordance with this mechanism one may expect that increased hydrogen pressure will bring to an accelerated cleaving of the alkyl group from the benzene nucleus. This was confirmed in isopropylbenzene: increasing the pressure from 200 to 600 atm (at 475[°]), the propane content of the hydrocarbon products increased from 21 to 59%.

As the pressure increases the rate of the gas phase reaction gradually deviates from calculated rates obtained from kinetic expressions derived for normal pressures. The classical theory of activated collisions explains this deviation on the basis of the decreasing free mean path between colliding molecules with increasing pressure until it becomes proportional