It may be noted that in one of the investigations mentioned above[23] interesting data were obtained on the effect of hydrogen pressure on the velocity of thermal cracking of paraffins. It was found that at low pressures of hydrogen the cracking was retarded, but a marked increase in the pressure of hydrogen led to some speeding-up of the process. Thus, for examples, the following results were obtained from the experiments with n-heptane:

Partial pressure of hydrogen (atm.)	$-^{x}$	250	640	1100
Yield (wt.-% of original heptane)				
(a) unreacted n-heptane	33.3	71.8	65.1	52.2
(b) gaseous and liquid products boiling below 48°C	37.7	20.5	27.5	38.5

Carrying out the cracking under a pressure of hydrogen prevents not only polymerisation reactions, but also destructive alkylation. It appears that this also provides an explanation for the increased proportion of unreacted n-heptane found on carrying out the process under 250 atm. of hydrogen, in comparison with thermal cracking in the absence of hydrogen. It may be supposed that the reason for the increased cracking on further increasing the pressure of hydrogen is that part of the hydrogen enters the reaction chain according to the equations:

$$R_1 + H_2 \longrightarrow R_1H + H;$$

$$H + R_oH \longrightarrow R_o + H_2.$$

A similar acceleration of the thermal decomposition of hydrocarbons as the partial pressure of hydrogen is increased (from 200 to 400 mm. Hg.) has recently been observed in the case of propane[27].

Thus, the use of high pressures for investigating the mechanism of the thermal cracking of paraffins has proved fruitful, and has allowed an explanation of some new features of this process.

B)   Homogeneous Destructive Hydrogenation of Aromatic Hydrocarbons.

When the kinetics of the homogeneous destructive hydrogenation of toluene under a high pressure of hydrogen was first investigated,[28] it was found that the velocity of this reaction is independent of the metal packing and in the first approximation may be expressed by the equation for a bimolecular reaction between toluene and hydrogen. The experimentally determined value of the energy of activation was 66,000 cal/mole; the pre-exponential term of the Arrhenius equation was found to be 60 times larger than that calculated from the theory of active collisions.

A recent investigation of the homogeneous destructive hydrogenation of toluene at 455-490°C. with pressures of hydrogen up to 1350 atm. led to the following results[29]:

a) The velocity of the reaction (as followed by the yield of benzene) increases with increasing hydrogen concentration, but somewhat less than proportionally. Thus, when the concentration of hydrogen was increased 3.8 times, the velocity of the reaction increased about 2.5 times.

b) The reaction velocity is approximately proportional to the square root of the toluene concentration.

c) The surface area of the wall of the reaction vessel and the surface area/volume ratio have no significant effect on the reaction velocity.

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* In the absence of hydrogen under a total pressure of 130 atm.