The radicals produced by reaction (2) may in turn react with molecules of the original hydrocarbon, thereby continuing the chain reaction:

$$R_1 + R_oH \xrightarrow{k_3} R_o + R_1H \qquad (3)$$

(see the right-hand part of equation 1).

Finally, the chain may be terminated, either on the wall of the reaction vessel (k_4)*, or by reaction (recombination or disproportionation) of the radicals R_o (k_5), R_o and R_1 (k_6) and R_1 (k_7).

On the basis of this scheme we obtain the following equation for the rate w of the cracking process, referred to the concentration of the original hydrocarbon (R_oH):

$$\frac{w}{(R_oH)} = \frac{2k_1k_2}{k_4 + \left[k_5 + \frac{k_2k_6}{k_3}\cdot\frac{1}{(R_oH)} + \frac{k_2^2k_7}{k_3^2}\cdot\frac{1}{(R_oH)^2}\right](R_o)}, \qquad (IV)$$

where round brackets denote concentrations.

Analysis of equation(IV) for various cases of selective reaction-chain-breaking leads to the following results:

a) When reaction chains normally terminate on the walls, the velocity of the reaction (in the units indicated) does not depend on the pressure (if we do not take into account the effect of pressure on the value of the rate constant). Consideration of the change in the velocity constant leads to the conclusion that the reaction is negligibly retarded by an increase in the pressure.

b) When reaction chains mainly end on radicals of the original hydrocarbon, the reaction is retarded by pressure:

$$\frac{w}{(R_oH)} = \sqrt{\frac{2k_1}{k_5}}k_2(R_oH)^{-\frac{1}{2}} . \qquad (V)$$

c) when reaction chains mainly terminate on short radicals, the reaction is accelerated by pressure:

$$\frac{w}{(R_oH)} = \sqrt{\frac{2k_1}{k_7}}k_3(R_oH)^{\frac{1}{2}} . \qquad (VI)$$

d) when reaction chains mainly finish by reaction of R_o with R_1 the rate of reaction is independent of pressure.

The results given here lead to the conclusion that at low pressures the breaking of reaction chains in the thermal cracking takes place mainly by reaction of "short" radicals (R_1), while at high pressures it is mainly due to reactions of "long" radicals (R_o). This assumption is confirmed by inspection of the ratio of the probabilities (δ) of these two ways of chain-breaking:

$$\frac{\delta(R_o)}{\delta(R_1)} = \frac{k_3^2\cdot k_5}{k_2^2\cdot k_7}(R_oH)^2 . \qquad (VII)$$

It follows from equation (VII) that the ratio of the probabilities of chains terminating on R_o and on R_1 is proportional to the square of the concentration of the original hydrocarbon, i.e. it increases very rapidly with an increase in pressure, which is a qualitative confirmation of the hypothesis given above. An approximate quantitative treatment of this question[25] also led to the conclusion that an increase in pressure, say from 5 to 500 atm., can cause the indicated change in the chain-breaking process.**

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* k = velocity constant.

** Analysis of the effect of pressure on the value of the velocity constant itself does not alter this conclusion.