MECHANISM OF THERMAL CRACKING OF NORMAL PARAFFINS

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Studies of the thermal cracking of the lower paraffin hydrocarbons have shown the presence of a retardation of the process by the reaction products [1-3]. In treatment of experimental results from cracking normal paraffins with a longer chain (n-octane or dodecane) at atmospheric pressure, A. V. Frost also indicated [4] a decrease in rate constant with degree of cracking. However, in his treatment he employed a kinetic equation for a monomolecular reaction in a closed system (at constant volume), while the experiments were conducted in a flow apparatus. A. S. Kazanskaya [5], and G. M. Panchenkov and V. Ya. Baryanov [6], on treating results of cracking n-octane and n-hexadecane in a flow apparatus at atmospheric pressure according to the equation derived by G. M. Panchenkov [7], found that the rate constant does not depend on the degree of conversion of the original hydrocarbon. Thus, although a retardation of cracking by the decomposition products (and by additions of propylene, isobutylene or nitric oxide) has been established indisputably for the lower paraffinic hydrocarbons, a retardation by the cracking products is apparently absent for normal paraffins with long chains.

In the cracking of normal paraffin hydrocarbons with a longer chain length (C_6 and above), significant quantities of C_4 and higher α-olefins (about 20% of the cracking products) are formed. The C−C bond in the olefin molecule which is conjugated with the double bond has a breaking energy of about 62 kcal/mole [8], and chain initiation as a the result of olefin decomposition should occur with a greater velocity than that from decomposition of the starting hydrocarbon by a factor of $e^{(74000-62000)/RT}$ (the breaking energy of the weakest C−C bond is 76 kcal/mole for C_6H_{14}, 75 kcal/mole for C_7H_{16}, or 74 kcal/mole for C_8H_{18}). At a temperature of 800°K, the rate of chain initiation on olefin decomposition should be greater than that from decomposition of the original paraffin when the concentration of C_4 and higher olefins is more than approximately 0.05%, which corresponds to a degree of conversion of about 0.25%.

On chain termination in olefin molecules as a result of formation of inactive allyl radicals, a simplified process scheme is represented in the following manner:

$$1.\ M \longrightarrow R + R_2;\quad K_1 \approx 10^{13} e^{-\frac{62000}{RT}}\ \text{sec}^{-1};$$

$$2.\ R + A \longrightarrow RH + R_1;\ K_2 \approx 10^{-13} e^{-\frac{9\,000}{RT}}\ \text{cm}^3 \cdot \text{sec}^{-1};$$

$$3.\ R_1 \longrightarrow M + R;$$

$$4.\ R + M \longrightarrow RH + R_2;\ K_4 \approx 10^{-14} e^{-\frac{6000}{RT}}\ \text{cm}^3 \cdot \text{sec}^{-1}$$

$$5.\ 2R_2 \longrightarrow \text{products of recombination or disproportionation.}$$

Here M represents C_4 or higher olefins (we neglect propylene); A is the starting hydrocarbon; R is CH_3 or C_2H_5; and R_2 represents radicals of the allyl type, formed on abstraction of a hydrogen atom from the olefin molecule at the weakest C−H bond.

Values of the activation energy were estimated according to the Polyani-Semenov rule [9]; the value of the steric coefficient is known [10] for reaction (2); for reaction (4) we accept a value of the steric coefficient an order of magnitude less than for reaction (2), from statistical considerations.

The ratio of rate of chain termination by reaction (4) to the rate of chain termination by recombination of active R radicals is given by the following:

$$\frac{V_4}{V} \approx \frac{10^{-14} \cdot e^{-\frac{6000}{RT}} \cdot [R]\,[M]}{P \cdot 10^{-10} [R]^2} = \frac{10^{-4}}{P} \cdot e^{-\frac{6000}{RT}} \cdot \frac{[M]}{[R]}\,.$$

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According to the calculations of A. D. Stepukhovich [11], the steric coefficients of the radical recombination reactions for 2 CH_3, $CH_3 + C_2H_5$, and 2 C_3H_5 have orders of magnitude of 10^{-3}, 10^{-4} and 10^{-6} respectively. Let us take $P = 10^{-4}$, then at 800°K, $V_4/V \approx 10^{-2} \cdot [M]/[R]$ and when $[M] > [R] \cdot 10^{-2}$, chain termination according to reaction (4) predominates. Consequently, even at a very low degree of cracking, chain termination takes place according to Eq. (4). If the steric coefficient of the radical recombination reaction is equal to 1, then $V_4 > V$ when $[M] > [R] \cdot 10^6$. The concentration of active radicals has an order of magnitude of 10^{11} per cc at 800°K and when $[M] > 10^{17}$ (1% at atmospheric pressure), chain termination is determined by reaction (4).

In such a process scheme, the cracking rate at a steady reaction course is equal to the following:

$$\frac{d[A]}{d\tau} = K_2[R]\cdot[A] = \frac{K_1K_2}{K_4}\cdot[A] \approx 10^{14}\cdot e^{-\frac{65000}{RT}} \tag{3}$$

The reaction takes place as a first order reaction, and its rate does not depend on olefin concentration.

The expression obtained for the rate of cracking of normal paraffins agrees well with the experimental data of [12].

Thus, the formation of C_4 and higher olefins on decomposition of normal paraffinic hydrocarbons should both inhibit and also accelerate the process, and their inhibiting action is overlapped by the facilitation of chain initiation on decomposition at the C—C bond conjugated with the double bond. Since chain generation of olefin decomposition and chain termination as a result of allyl radical formation should predominate even at very low olefin concentrations, it is difficult to determine experimentally the effect of degree of cracking on cracking rate for C_6 and higher paraffinic hydrocarbons; all the available kinetic data in the literature on cracking of C_6 and higher normal paraffins apparently describe an "accelerated" process.

The compensation of the inhibiting action of n-butylene by the facilitation of chain initiation on its decomposition is explained evidently by an absence of an effect of n-butylene addition on the cracking rate [13, 14].*

When paraffins of small chain length are cracked, C_4 and higher olefins are practically not formed, because of which only the retarding action of propylene is manifested.

CONCLUSIONS

1. It has been shown that in the cracking of normal paraffins with a long chain, the retarding action of the olefins formed is compensated or even overcome as a result of formation of radicals from decomposition of the olefins at the C—C bond conjugated with the double bond.

2. Cracking of normal paraffins having long chains, beginning at a very low degree of cracking, about 0.1%, takes place as a chain process with chain generation as a result of decomposition of C_4 and higher olefins.

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*No reference to [14] appears in Russian original—Publisher's note.