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Abstract

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ON RADIATION-THERMAL CRACKING OF HYDROCARBONS

At the present time the possibility of industrial application of radiation cracking is determined primarily by the following factors: a) the possibility of initiating by radiation a chain reaction with an acceptable chain length; b) the possibility of obtaining, in high yield and in a readily separable mixture, products of special interest (in particular, unsaturated hydrocarbons).

The solution of this problem is possible by developing radiation-thermal cracking (r.t.c.), in which the radiation creates centers initiating the reaction, while the temperature removes the activation barriers that hinder chain development.

In our work ([1,2]) and in the work of other authors ([3]) it has been shown that the total yield of hydrocarbon radiolysis products at room temperature is of the order of 10 molecules per 100 eV, which is one indication of the absence of a chain reaction under these conditions. The reaction proceeds mainly toward dehydrogenation (by various mechanisms) of the initial molecule, so that the gaseous products of heptane radiolysis contain about 80% hydrogen. Although hydrogen itself, as is known, is a very valuable product for various chemical purposes, nevertheless, at yields not exceeding 5 molecules per 100 eV, there is no reason to speak of the advisability of its industrial production by this method. Among the remaining 20% of gaseous radiolysis products there are both saturated "fragment" hydrocarbons and unsaturated ones; moreover, whereas the accumulation of hydrogen is linear over a very considerable range of integral doses, for the products of C–C bond rupture nonlinearity begins at comparatively small doses and is manifested more strongly for unsaturated gases than for saturated ones, as a result of which the percentage of unsaturated compounds in the gas rapidly decreases. The amount of liquid unsaturated compounds is approximately one-half the total amount of hydrogen formed (in the linear region). These unsaturated compounds are mainly trans- and α-olefins formed during dehydrogenation of the initial molecule. The amount of diene compounds is about two orders of magnitude less than that of liquid monoolefins.

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

To determine the possibility of carrying out a chain reaction of radiation cracking, it was necessary to pass to higher temperatures and, consequently, to conduct experiments in the vapor phase. In our experiments (^{1,2}) on irradiation of liquid *n*-heptane with Co^{60} γ-radiation, the dose rate was $4 \cdot 10^{15}$ eV/sec • ml. When alkane vapors are irradiated, because of the substantial difference in densities, the maximum attainable dose rate is reduced by 2–3 orders of magnitude in comparison with the liquid. To shorten substantially the duration of experiments on radiolysis of alkane vapors at significant dose rates, an electron beam of 900 keV was used, produced by an accelerator consisting of a vertical sectioned direct-acceleration tube and a cascade valve-capacitor voltage multiplier (^{4}).

Alkane samples were irradiated in molybdenum-glass bulbs with a wall thickness of ~ 1 mm and a volume of ~ 15 ml. The usual amount of liquid heptane during irradiation was 0.25 ml; upon evaporation the pressure in the ampoules was $2.5\,T/273$ atm. A vertical electron beam struck the upper wall of the bulb, which was placed in a furnace. To prevent local heating of the wall and to create more uniform irradiation conditions, the bulb was rotated at a speed of 2 rev/sec. The temperature was measured with a thermocouple attached externally to the wall of the bulb. The course of the reaction was monitored remotely by means of a television setup. To determine the true dose rate in the irradiated volume, a method of chemical dosimetry was used, based on determination of the loss of acetylene pressure as a result of its radiation-chemical polymerization (^{5}). Acetylene dosimetry at room temperature gave a dose-rate value in 1 cm^3 of the reaction-vessel volume of $2.7 \cdot 10^{15}$ eV/sec for an initial number of acetylene molecules of $1.4 \cdot 10^{19}$ in 1 cm^3. Taking into account the difference in electron densities of *n*-heptane and acetylene, the number of *n*-heptane molecules in our experiments, and the differences in current strength during acetylene dosimetry and during irradiation of *n*-heptane, we obtain a dose rate of $2 \cdot 10^{19}$ eV/sec, calculated per 1 ml of liquid *n*-heptane.

Fig. 1. Kinetics of accumulation of radiolysis products of *n*-heptane at 200°. 1 —hydrogen; 2 —liquid olefins; 3 —methane

Fig. 2. Dependences of the radiation-chemical yield of hydrocarbons of the C_2 —C_5 fraction (1) and methane (2) on the temperature of r.t.c.; 3 —dependence of the percentage of unsaturated hydrocarbons in the C_2—C_5 fraction on the temperature of r.t.c.

It was shown that the formation of hydrogen, methane, and unsaturated compounds deviates from linearity only at large integral doses (Fig. 1). A blank experiment at 350° without exposure to radiation showed that, owing to the purely thermal reaction, less than 1/3 of the products of the C_2—C_5 fraction is

Figure 3 and Figure 4

Figure 2: Figure 3 and Figure 4

formed. In the case of r.t.c., the content of unsaturated compounds in this fraction increases to 56% as compared with 30% in the case of the purely thermal reaction.

When the data for r.t.c. carried out under the action of γ-radiation from Co^{60} and 900 keV were compared, no noticeable differences were found.

Figure 2 shows the dependences of the radiation-chemical yield of methane and hydrocarbons of the C_2–C_5 fraction on the temperature of r.t.c. As is seen from Fig. 2, the relatively slow increase in the yield of the C_2–C_5 fraction at temperatures below $\sim 300^\circ$ is replaced by an extremely steep rise. The temperature dependence of the methane yield is analogous. At the same time, the percentage of unsaturated hydrocarbons in the C_2–C_5 fraction increases, reaching 62% at 400°.

R. t. c. of *n*-heptane proceeds at temperatures significantly lower than purely thermal cracking of heptane, which proceeds at an appreciable rate at temperatures of $\sim 500^\circ$. The yield of liquid unsaturated compounds, determined from the bromine numbers of the liquid after removal of the gas fractions, increases from 2 molecules per 100 eV at room temperature to 340 at 450° (Fig. 3). These facts, together with the constancy of the rate of r. t. c., allow one to suppose that the r. t. c. process proceeds with the participation of direct unbranched chains, in accordance with the generally accepted concepts of the mechanism of thermal cracking.

Figure 4 presents the dependence of the logarithm of the product yield on the reciprocal of the absolute temperature. From the break in the logarithmic curve it is clearly seen that, beginning at temperatures of $\sim 230^\circ$, the formation of methane and other hydrocarbon gases proceeds, for the most part, by a different mechanism than at lower temperatures. In this case, whereas at low temperatures the temperature dependence of the yield of methane (and similarly of the C_2—C_5 fraction) corresponds to an activation energy < 1 kcal/mol, at high temperatures the activation energy is ~ 18 kcal/mol, which agrees satisfactorily with the known values of the activation energy of chain propagation in thermal cracking (6). The latter value, evidently, should determine the magnitude of the effective activation energy of r. t. c., since initiation of the reaction

Fig. 3. Dependence of the radiation-chemical yield of liquid olefins on the temperature of r. t. c.

Fig. 4. Dependence of the logarithm of the radiation-chemical yield of methane (1), hydrogen (2), and hydrocarbons of the C_2—C_5 fraction (3) on the reciprocal temperature of r. t. c.

occurs mainly by radiation, while the most energy-consuming step remains the chain-propagation reaction.

From the foregoing it follows that at a temperature of 400° the total radiation-chemical yield of low-molecular-weight hydrocarbon products is $\sim$ 2000 molecules per 100 eV, i.e., it increases by $\sim 10^3$ times in comparison with the radiation-chemical yield of these same products from the radiolysis of heptane vapors at 20°.

Of considerable interest is the performance of r. t. c. at the temperatures of thermal cracking, which we are currently studying.

A similar increase in yields was noted in studying the effect of γ-radiation and reactor radiation on the thermal cracking of n-hexadecane and petroleum fractions ([7]). Such yield values, with a simultaneous increase in the percentage content of unsaturated products, are of direct practical interest.

Thus, by combining radiation exposure and temperature, it is possible to obtain both practically acceptable yields and a composition of radiolysis products that is of practical interest.

The preliminary experiments we have carried out on r. t. c. of naphthenic hydrocarbons and petroleum also gave very promising results, analogous-

···as those set forth above. At present we have developed and are testing an apparatus for carrying out radiation-thermal cracking of vapors of liquid hydrocarbons and low-molecular hydrocarbon gases in a flow system.

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