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Abstract

Full Text

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On the Thermal Stability of Synthetic Hydrocarbons C_{32} of Hybrid Structure

In studying the properties and structure of hydrocarbons of the high-molecular-weight portion of petroleum, it is necessary, for comparison, to have synthetic structural types of hydrocarbons that to some extent model them. Since among the high-molecular-weight hydrocarbons of petroleum hybrid structures predominate, i.e., compounds that contain two or more structural elements—for example, a paraffin chain and rings of different structure (penta- and hexamethylene, benzene, naphthalene, decalin, tetralin rings)—we synthesized a considerable group of such synthetic models of hydrocarbons of hybrid structure ([1–3]). The viscosity-temperature and some other basic properties of these hydrocarbons ([4,5]) were studied. Their adsorption properties were studied in detail ([6]).

The absorption spectra of these hydrocarbons in the infrared ([7]) and ultraviolet ([8]) regions were also studied and described for the first time. All these data now greatly facilitate the solution of a rather difficult problem—the study of the chemical nature of hydrocarbons in the heavy portion of petroleums, among which molecular structures of the hybrid type predominate. For solving a number of technical problems it is very important to know the thermal stability of these hydrocarbons.

Fig. 1. Schematic thermogram: $-Q$—processes proceeding with heat absorption, $+Q$—the same, with heat evolution.

Of special interest are high-viscosity oils obtained from high-boiling fractions of petroleum. High-boiling petroleum fractions are also subjected to thermal and catalytic cracking. The C_{32} hydrocarbons synthesized by us fall within the indicated region. The number of hydrocarbons present in high-boiling petroleum fractions is extremely large, and it is practically impossible to synthesize them all one after another. However, it is possible to carry out selective syntheses of types of hybrid hydrocarbon structures analogous to petroleum hydrocarbons.

By combining several structural units in molecules, one can reproduce the full diversity of structure and properties of high-molecular-weight hybrid hydrocarbon molecules of petroleum and use these data to judge the composition and properties of high-molecular-weight fractions of petroleums. Individual cyclic units of hybrid hydrocarbon molecules, having a definite number of substituents, are joined to one another by means of paraffin chains of different length and branching, forming complex hydrocarbon molecules. Depending on the structure, number, and mutual arrangement of the aliphatic and cyclic structural units in the molecule, the physical properties and chemical reactions of the hydrocarbons will manifest themselves.

We synthesized model high-molecular-weight hydrocarbons in order to clarify only part of the first stage of the general problem, i.e., the influence of the number and mutual arrangement of benzene, naphthalene, tet-

Table 1

Thermographic data for synthetic individual hydrocarbons C_{32}

Hydrocarbon	Onset of decomposition process, °C	Compaction processes, °C: onset	Compaction processes, °C: end
$C_{11}H_{23}-CH(C_{10}H_{21})_2$	390	415	440
$C_{11}H_{23}-CH(C_{10}H_{21})-$naphthalene ring	385	405	440
$C_{11}H_{23}-CH(C_{10}H_{21})-$tetralin ring	385	405	430
$C_{11}H_{23}-CH(C_{10}H_{21})-$decalin ring	385	420	450
$C_{11}H_{23}-CH-$naphthalene ring; substituent: decalin ring	385	420	450
$C_9H_{19}-CH-CH_2-$tetralin ring; substituent: CH_2-tetralin ring	395	420	480

Hydrocarbon	Onset of decomposition process, °C	Compaction processes, °C: onset	Compaction processes, °C: end
$CH_3-CH-(CH_2)_8-CH-CH_3$; each CH bearing a decalin ring	375	420	480
$C_{13}H_{27}-CH-CH_2-$cyclohexane ring; CH bearing a decalin ring	390	420	470
$C_{13}H_{27}-CH-CH_2-$benzene ring; CH bearing a naphthalene ring	385	415	470
$C_{13}H_{27}-CH-CH_2-$benzene ring; CH bearing a tetralin ring	385	415	450
$C_{13}H_{27}-CH-CH_2-$benzene ring; CH bearing a naphthalene ring	385	415	470
$C_{13}H_{27}-CH-CH_2-$benzene ring; CH bearing a decalin ring	400	405	450

tetralin, decalin, and cyclohexane rings. As studies of viscosity and adsorption properties have shown, there is a definite dependence, for each phenomenon, on structure ([2,6]). In the present communication, using synthesized hybrid high-molecular hydrocarbons as examples, the dependence of thermal stability on the structure of hydrocarbons is shown (Table 1). The thermal stability was determined on a Kurnakov pyrometer. Two quartz cups were placed in the metal block of the pyrometer: one contained 0.1–0.2 g of the hydrocarbon under

Fig. 2. Thermogram of 1,1-dinaphthyl-dodecene-1

Figure 2: Fig. 2. Thermogram of 1,1-dinaphthyl-dodecene-1

Fig. 3. Thermogram of 11-α-naphthyldocosane: 1 —on aluminosilicate catalyst, 2 —without catalyst

Figure 3: Fig. 3. Thermogram of 11-α-naphthyldocosane: 1 —on aluminosilicate catalyst, 2 —without catalyst

study, and the other contained aluminum oxide. Heating was carried out in a special furnace under a constant electrical load, which ensured a uniform rise in temperature. Using a differential thermocouple and mirror galvanometers, the temperature of the sample and the temperature difference in the two cups were recorded simultaneously on photographic paper. This made it possible to mark the processes occurring in the sample with the evolution or absorption of heat. On the basis of the thermograms obtained, graphs were constructed which, for all the limiting hydrocarbons, have the form shown in Fig. 1. The straight line up to point A shows that, in this temperature interval, no processes accompanied by the evolution or absorption of heat occur in the sample. In the interval between points A and B, an endothermic effect is observed, i.e., the process proceeds with absorption of heat. Between points B and C, a strong exothermic effect appears; the process proceeds with evolution of heat. After the maximum of the exothermic effect at point C, a slight endothermic-

···effect, after which the temperature curve becomes flatter and then runs parallel to the abscissa axis.

Point A, at which the process accompanied by heat absorption begins, probably characterizes the onset of the endothermic cracking processes. The condensation processes (polymerization and condensation), which proceed with evolution of heat, begin at point B. The starting material for the exothermic condensation processes is radicals and reactive unsaturated molecules formed during the destruction (cracking) of the initial hydrocarbons. The segment of the thermographic curve to the right of point C characterizes the parallel course of cracking and condensation processes, with some predominance of the former. The data obtained for a number of individual hydrocarbons are summarized in Table 1.

Fig. 2 shows the thermographic curve of 1,1-dinaphthyl-dodecene-1, from which it is clearly seen that the presence of a double bond in the molecule causes the exothermic process (polymerization) to occur earlier than the endothermic cracking process. In the case of saturated hybrid hydrocarbon structures (Fig. 1), on the contrary, the endothermic process (cracking) always precedes the exothermic one (polymerization).

Fig. 2. Thermogram of 1,1-dinaphthyl-dodecene-1

Fig. 3. Thermogram of 11-α-naphthyldocosane: 1 —on aluminosilicate catalyst,

2 —without catalyst

Fig. 3 presents thermograms of 11-α-naphthyldocosane in the presence of an aluminosilicate catalyst and without a catalyst. The experiment for recording the thermogram of the hydrocarbon with catalyst was carried out as follows. The catalyst was ground to powder in an agate mortar, mixed with the hydrocarbon, and placed in a beaker in the form of a paste. A second beaker was filled with pure aluminosilicate catalyst. In this way the thermal processes occurring in the catalyst itself are excluded. The study of the thermal stability of hybrid hydrocarbon structures C_{32}, containing in the molecule benzene, naphthalene, cyclohexane, and decalin nuclei, showed that in this respect they differ little from the paraffinic hydrocarbon 11-undecylheneicosane; in all of them the endothermic effect (decomposition) appears in the temperature interval 385—400°, and the exothermic effect (condensation processes) in the interval 405—470°. When an olefinic bond is present in the hydrocarbon molecule, the endothermic and exothermic effects on the thermogram change places; the exothermic effect (polymerization) appears at $\sim 370°$. This may serve as a qualitative indicator of the presence of olefins in hydrocarbon mixtures.

In the presence of an aluminosilicate catalyst, an exothermic effect appears on the thermogram of saturated hybrid hydrocarbon structures C_{32} in the temperature interval 220—245°. It evid—

indicates, probably, the occurrence of an exothermic process of chemisorption.

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Note: Figure translations are in progress. See original paper for figures.