PHYSICAL CHEMISTRY

A. M. BRODSKII, Corresponding Member of the Academy of Sciences of the USSR, K. P. LAVROVSKII, and V. B. TITOV

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Abstract

Full Text

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ON RADIATION-THERMAL CRACKING OF LIQUID HYDROCARBONS

This paper considers the effects of the combined action of high-energy radiation and heating on natural mixtures of hydrocarbons—gas-oil fractions boiling within the range 200–350°. The experiments were carried out in heated evacuated quartz ampoules in a VVR reactor ([1,2]). The ampoules, filled with liquid to approximately one third of their volume, had an internal diameter of 10 mm and a length of 250 mm. Before sealing, the contents of the ampoule were thoroughly degassed. From the results of our experiments, in agreement with the results of work ([3]), it follows that in the radiolysis of liquid hydrocarbons the dependence of $\ln G$ (where G is the number of molecules undergoing destruction upon absorption of 100 eV of energy) on the reciprocal absolute temperature $1/T$ has the characteristic form shown in Fig. 1. Below a certain limiting temperature T_p, the value of G changes comparatively little with increasing T (regime I in Fig. 1). Beginning with the temperature T_p, amounting to approximately 600°K, the value of G begins to increase rapidly, with an activation energy of 20 ± 5 kcal (regime II). In this case the transition from regime I to regime II occurs very sharply, with a small smoothing transition section. With a further increase in temperature, regime II gradually passes into thermal cracking (regime III). In regime III the extent of decomposition ceases to depend only on the total absorbed energy dose, as in regimes I and II, and begins to depend substantially on the dose rate, i.e., on the residence time in the reaction zone.

Fig. 1. Schematic dependence of $\ln G$ on $1/T$; T_p is the critical point.

The existence of regime II in the radiolysis of hydrocarbon gases was first noted in the work of L. S. Polak et al. ([4]), and regime II was called radiation–thermal cracking. From the data of ([4]) one may conclude that, in the radiolysis of gaseous hydrocarbons, the dependence of G on temperature in regime I is practically absent, in contrast to the case investigated by us of the radiolysis of liquid products, where the corresponding activation energy is equal to several

kilocalories*.

As follows from our experimental data, the temperature dependence of the rate of formation of high-molecular products ("polymers") has an essentially different character. Figure 2 shows the dependence of $\ln G_{\text{h.m.}}$, where $G_{\text{h.m.}}$ is the number of molecules of the initial hydrocarbons converted into high-molecular products, on $1/T$ for the case of radiolysis of gas oils. The yield of high-molecular products was determined by us with the aid of so-called molecular distillation in a high vacuum (10^{-5} mm Hg). As can be seen from Fig. 2, beginning with the temperature T_p the radiation-chemical yield of high-molecular products from hydrocarbons of limiting structure begins to decrease rapidly.

* A change in the mechanism of hydrocarbon decomposition with increasing temperature was noted in the work of M. A. Mokul' skii ([7]); however, in that work radical reactions, which in our case are of principal importance, were not taken into account.

For interpreting the processes occurring during radiation-thermal decomposition, it is important that the temperature course of formation of the various low-molecular-weight destruction products is somewhat different. In Fig. 3 we present the dependences we have established of the radiation-chemical yields of low-molecular-weight destruction products on temperature.

The chemical effect of the interaction of radiation with hydrocarbon molecules can be reduced to processes of two types, which may proceed independently of one another:

$$\begin{gathered}\text{hydrocarbon} + \text{radiation} \rightarrow \ldots \\ \ldots \rightarrow \text{excited molecule} \rightarrow \text{final stable products}\end{gathered} \tag{1}$$

$$\begin{gathered}\text{hydrocarbon} + \text{radiation} \rightarrow \ldots \\ \ldots \rightarrow \text{thermal hydrocarbon radicals} \rightarrow \text{products of radical reactions}\end{gathered} \tag{2}$$

Processes (1) correspond to the so-called direct path of radiation-chemical transformations, and processes (2) to the radical path. At the same time, for the further discussion there is no need to establish detailed mechanisms of the intermediate stages of the reactions indicated in (1) and (2) by ellipses. These intermediate stages, possibly including the formation of ions or hot radicals, have not yet been fully clarified. What is essential is that in the temperature interval under consideration, which includes the regimes I and II indicated above, the rate of formation of final products through processes (1) should not depend noticeably on temperature, since the excitation energies in (1) in this interval are significantly greater than kT. Thus, processes (1) make an identical, temperature-independent contribution to hydrocarbon decomposition under regimes I and II.

Fig. 2. Dependence of the radiation-chemical yield of the high-molecular-weight residue on temperature

Fig. 2

Figure 2: Fig. 2

The subsequent behavior of the hydrocarbon radicals formed in processes (2) is substantially different under regimes I and II. In the first case the radicals are stable and enter predominantly into recombination reactions with one another. Under regime II the aliphatic (or mixed) radicals that have formed decompose to a considerable extent, with formation of olefins and radicals of lower molecular weight, which enter into further substitution and decomposition reactions.

Let us define the temperature T_p at which regime I begins to pass into regime II. We first consider the case in which cage effects and analogous effects may be neglected. Such a case is realized, in particular, in the radiolysis of hydrocarbon gases. Here one may assume that radiation-thermal cracking will begin when the rate of radical decomposition reactions, equal to $k_d[\mathrm{R}]$, reaches the magnitude of the rate of reactions proceeding under regime I. Thus, at the temperature of transition from regime I to regime II (T_p) we have

$$k_d[\mathrm{R}] \simeq a_1 G_1 I, \tag{3}$$

where $k_d = k_d^0 e^{-E_d/RT_p}$ is the averaged rate constant of radical decomposition; [R] is the concentration of thermal high-molecular-weight radicals formed in reaction (2); G_1 is the radiation-chemical yield of reaction (1); I is the dose rate of irradiation absorbed per unit volume; and a_1 is a numerical constant of order unity. The balance equation for high-molecular-weight radicals may be written (in the cases considered, the steady-state condition is fulfilled for the change in the concentration of active radicals)*:

$$IG_R - k_d[\mathrm{R}] - k_T[\mathrm{R}][\overline{\mathrm{R}}] = 0, \tag{4}$$

* Here it is taken into account that the consumption of radicals leads to the formation predominantly of a low-molecular-weight radical (CH_3, C_2H_5) and an olefin molecule.

where $[\overline{R}]$ is the total concentration of radicals, determined by the equation:

$$IG_{\overline{R}} - \overline{k}_T[\overline{R}]^2 = 0 \tag{5}$$

(G_R is the radiation-chemical yield of radicals R in reaction (2), and $G_{\overline{R}}$ is the total yield of radicals).

The values of the recombination constants k_T and $\overline{k}_T$ may be regarded as independent of temperature ([5]). In the subsequent estimate of T_p we shall put $\overline{k}_T \simeq k_T$. From formulas (4) and (5) it follows that

$$T_p = E_d/R \ln\left(k_d^0 b/\sqrt{k_T I G_{\overline{R}}}\right), \tag{6}$$

where the temperature-independent constant $b = (1 - a_1 G_1/G_R) > 0$ is close to unity and may be omitted. From formula (6) it is seen that T_p is practically independent of the choice of the value a_1, which is also related to the comparatively sharp transition from radiolysis to radiation-thermal cracking and to the weak dependence of T_p on inhibition, which changes the ratio G_R/G_1. The quantity T_p is proportional to E_d and changes little with a change in dose rate I. Substitution into (6) of the values: $G_{\overline{R}} \sim 5$ (per 100 eV), $k_T = 10^{-11}$ cm^3/mol sec, $k_d^0 = 10^{13}$ sec^{-1}, and $E = 25 \div 30$ kcal/mol ([5]) gives $T_p = 600^\circ$ K, in agreement with the experimental data mentioned above.*

Let us now examine the condition for transition from regime I to regime II in the case of liquids proper. In the first limiting case, if the cage effect may be neglected, the general expression (6) for T_p is preserved. It is necessary only to bear in mind that the value of k_T in a liquid is several orders of magnitude smaller than in gases ([6]). Somewhat smaller than in gases, owing to more rapid energy dissipation in a liquid, are also the quantities G_1, G_R, and $G_{\overline{R}}$, which, however, is usually compensated in formula (6) by the considerably higher values of the dose rate of energy absorbed per unit volume. In the second limiting case –of a strong cage effect**–the concentration of radicals $[\overline{R}]$ must be divided into two parts: $[\overline{R}] = [\overline{R}'] + [\overline{R}'']$ (with $G_{\overline{R}} \simeq G_{\overline{R}'}$), the first of which, $[\overline{R}']$, denotes the number of radicals per unit volume located in the cage in pairs, next to another radical with which they were formed together, and $[\overline{R}'']$ is the concentration of high-molecular radicals that have found themselves outside the cages as a result of radical diffusion. The balance equation for radicals $\overline{R}'$ may be written in the form

$$G_{\overline{R}'} I - 1/\tau_T [\overline{R}'] - k_d [\overline{R}'] = 0, \tag{7}$$

Fig. 3. Dependence of the radiation-chemical yields of certain gaseous radiolysis products on temperature (E–activation energies of the processes, in kcal/mol). 1–hydrogen, $E = 0.5$ (regime I), $E = 3$-4 (regime II); 2–methane, $E = 2$ (regime I), $E = 20$ (regime II); 3–propane, $E = 4$ (regime I), $E = 12$-13 (regime II); 4–propylene, $E = 2$-3 (regime I), $E = 13$-14 (regime II); 5–n-butane, $E = 4$ (regime I), $E = 12$-13 (regime II).

$$\lg G_i \uparrow \qquad 1000/T \longrightarrow$$

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* The increase in T_p with increasing I is a consequence of the circumstance that, with increasing dose rate, the rate of reactions (1) increases faster than the rate of reaction (2).

** The structural formation in a liquid, called a "cage," is understood in the sense of ([8,9]).

where τ_T is the time for the decrease of $[\overline{\mathrm{R}}']$ due to recombination by a factor of e. In the limiting case considered, we neglect the diffusion of radicals in the balance equation (7). At temperatures approaching T_p, the balance equation for $\overline{\mathrm{R}}''$ takes the form

$$1/\tau_D[\overline{\mathrm{R}}'] - k_d[\overline{\mathrm{R}}''] - k_T[\overline{\mathrm{R}}]^2 = 0, \tag{8}$$

where $1/\tau_D$ is the reciprocal diffusion time of radicals out of the cells.

From (7) and (8) we obtain that the rate of destruction processes with formation of olefins in this case is equal to (the direct processes (1) may be neglected here)

$$G_{\text{olefins}}I = k_d[\overline{\mathrm{R}}] = k_d\left([\overline{\mathrm{R}}'] + [\overline{\mathrm{R}}'']\right) \simeq (k_d + 1/\tau_D)G_{\mathrm{R}'}I(1/\tau_T + k_d)^{-1} \tag{9}$$

(recombination outside the cells in (9) is omitted in view of the comparative smallness of the corresponding steric factors in the liquid).

It follows from formula (8) that at temperatures for which $k_d \ll 1/\tau_D \ll 1/\tau_T$, the temperature dependence of destruction reactions will be comparatively weak. The corresponding activation energy must be equal to the activation energy of diffusion of light radicals leaving the cell. This latter circumstance explains why, in regime I of radiolysis in a liquid, there occurs some acceleration of the formation of destruction products, and this acceleration is the smaller, the lower the molecular weight of the given product (see Fig. 3). According to (9), a rapid increase in the rate of destruction processes, i.e., the transition from regime I to regime II, will occur at the same temperature at which

$$k_d = k_d^0 \exp(-E_d/RT_p) \simeq 1/\tau_D \tag{10}$$

and will not depend on the dose rate. In regime II, when $k_d \gg 1/\tau_D$, the temperature dependence of radiolysis will be determined by the temperature dependence of the factor $k_d/(1/\tau_T + k_d) \simeq k_d\tau_T$, since for the most part $k_d \ll 1/\tau_T$. Formula (10) makes it possible to estimate the sizes of the cells from expressions for the kinetic constants and from experimental data on radiolysis at different temperatures.

Let us apply the above considerations to the case of radiolysis of gas oil. As follows from examination of Fig. 3 and from simple kinetic considerations, the

activation energy of destruction of high-molecular radicals with formation of the CH_3 radical, which is then converted into CH_4, is ~ 20 kcal. Substituting $E = 20$ kcal/mole into expression (10) and taking $k_d^0 = 10^{13}$ sec^{-1}, $1/\tau_D = D/d^2$, where d is the cell size, $T_p = 600°$K, we find, for $D = 10^{-5}$ cm^2/sec, that $d = 10^{-6}$ cm. From the data presented it may be concluded that the cell effect is quite significant in the radiolysis of liquid hydrocarbons. We note that the increase in polymer yield in regime I, visible from Fig. 2, with an activation energy close to the activation energy of diffusion, confirms this proposition. In conclusion, let us emphasize that the study of regime II (radiation-thermal cracking) may prove to be an important and very simple means of determining detailed characteristics of a number of elementary acts of chemical reactions.

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

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