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Abstract

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STUDY OF THE RADIOLYSIS OF HYDROCARBONS BY SPECTRAL METHODS

In studying the radiolysis of hydrocarbons, the greatest difficulties are presented by the qualitative and quantitative determination of its products in the liquid phase. Considerable assistance in this respect is provided by the study of absorption spectra in the ultraviolet and infrared regions.

In the radiolysis of alkanes, the principal process that occurs is the rupture of C—H bonds—the process of dehydrogenation; in this process, H_2 accumulates in the gas phase, while in the liquid phase there are various radiolysis products, depending on whether atomic or molecular hydrogen is split off from the original alkane molecule. The removal of atomic hydrogen leads to the formation of the radical C_7H_{15}, which enters into subsequent reactions, whereas removal of a hydrogen molecule gives, in the liquid phase, a residue in the form of heptene; removal of $2H_2$, with closure of two double bonds, should lead to the formation of dienes, which subsequently actively dimerize and polymerize.

The method of studying ultraviolet absorption spectra makes it possible to establish the presence of conjugated dienes in the radiolysis products, while the method of infrared absorption spectra makes it possible to establish the presence of compounds with an ethylenic bond (heptenes, etc.); it is also possible to identify a number of other features of the radiolysis products.

The radiolysis of alkanes under the action of γ-radiation was studied by us using installations employing Co^{60} γ-radiation of nominal strength 1400 and 20,000 Cu. Irradiation was carried out in evacuated, deoxygenated, and sealed glass ampoules. After the ampoules were opened, the gaseous and liquid phases of the radiolysis products were studied separately. The main part of the work was done with heptane, but several other individual normal alkanes available to us, isooctane, and cyclohexane were also studied.

Absorption spectra in the ultraviolet region were recorded on a spectrovisor with an attachment for automatic recording of absorption curves in the Optical Laboratory of the Institute of Organoelement Compounds of the Academy of Sciences of the USSR. As a rule, spectra were recorded in the region 30–45 $\cdot 10^3$ cm^{-1}, and in individual cases in the region 25–45 $\cdot 10^3$ cm^{-1}. Figure 1 presents some of the absorption curves obtained by us; for each curve the dose in millions of roentgens and the dilution of the sample are indicated. As can be

Fig. 1. Ultraviolet absorption spectra of irradiated hydrocarbons.

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seen, irradiated *n*-hexane, heptane, and octane have similar absorption curves with an absorption maximum in the region 40-44 $\cdot 10^3$ cm^{-1}. The spectrum of irradiated isooctane is very close to the spectrum of irradiated octane. In the spectrum of irradiated dodecane, and to an even greater extent that of irradiated cetane, in addition to the indicated band another band appears in the longer-wavelength region. The spectrum of irradiated cyclohexane differs from the spectrum of hexane and other normal hydrocarbons that received a dose of 40 $\cdot 10^6$ r.

As is known, saturated hydrocarbons are typical transparent compounds in the region of interest to us, ~30-45 $\cdot 10^3$ cm^{-1} (in Fig. 1 the absorption of unirradiated hydrocarbons corresponds to the zero line),

whereas an isolated ethylenic bond absorbs in a considerably shorter-wavelength region than the region accessible to the instrument used.

By contrast, absorption by conjugated dienes is very intense and has a maximum ($\varepsilon \sim 20\,000$) in the interval ~ 42–$46 \cdot 10^3$ cm^{-1}, i.e., precisely in the region where the absorption maximum observed by us is found.

Thus, the absorption observed for irradiated alkanes in the indicated region should be attributed to the formation of conjugated dienes (and polyenes).

Fig. 1. Ultraviolet absorption spectra of irradiated hydrocarbons. **1** –*n*-heptane, dose $99 \cdot 10^6$ r, dilution 1 : 10; **2** –isooctane, dose $40 \cdot 10^6$ r, dilution 1 : 5; **3** –*n*-octane, dose $40 \cdot 10^6$ r, dilution 1 : 5; **4** –*n*-hexane, dose $34 \cdot 10^6$ r, dilution 1 : 5; **5** –*n*-dodecane, dose $40 \cdot 10^6$ r, dilution 1 : 10; **6** –*n*-cetane, dose $40 \cdot 10^6$ r, dilution 1 : 5; **7** –cyclohexane, dose $40 \cdot 10^6$ r, dilution 1 : 20.

The presence of aromatics in irradiated cyclohexane is beyond doubt. It is also confirmed by the usual method—the positive formalite reaction in irradiated cyclohexane (in the unirradiated material this reaction is negative).

When isooctane is irradiated, ten times more methane is obtained than when *n*-octane is irradiated, and the amount of hydrogen formed decreases correspondingly; this should also be reflected in a decrease in diene formation. And indeed, we have:

	Integral of the absorption area in the region $38 \cdot 10^3$–$45 \cdot 10^3$ cm^{-1}
n-Octane	25.50
i-Octane	20.45

Figure 2 gives the absorption curves in the ultraviolet region for three fractions

Fig. 2. Ultraviolet absorption spectra of fractions of irradiated heptane

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obtained by fractionation (without heating) of irradiated heptane. Fraction I is the lightest; IV is a heavy yellow residue with molecular weight ~ 200; the spectrum of fraction III, consisting mainly of heptane, is not presented. From consideration of the curves shown, it is evident that the absorption of the two light fractions is distinguished by a sharp boundary on the long-wavelength side and by a decrease in the region $42.5–45.5 \times 10^3$ cm^{-1} (these curves differ from one another only in absorption intensity; the dilution for fraction I is 1 : 40, and for II 1 : 10). The observed absorption can belong only to conjugated dienes (probably, chiefly heptadienes, which in volatility scarcely differ from heptane).

Examination of the spectrograms in Fig. 2 allows us to suggest that, in the course of heptane radiolysis, alongside other transformations, dehydrocyclization with the formation of toluene is possible. This question will be subjected by us to further careful experimental study.

The absorption curve of the heavy residue (which, unlike the initial heptane, fluoresces intensely under illumination with ultraviolet light) gives a picture of continuous, steadily increasing absorption from $35 \cdot 10^3$ to $45 \cdot 10^3$ cm^{-1} (one must bear in mind the enormous dilution 1 : 100). Here, evidently, in addition to conjugated dienes, polyenes also absorb, and probably all sorts of dimers and polymers formed as a result of secondary reactions with dienes and polyenes.

Fig. 2. Ultraviolet absorption spectra of fractions of irradiated heptane (dose $137 \cdot 10^6$ r).
1 –fraction I, dilution 1 : 40; 2 –fraction II, dilution 1 : 10; 3 –fraction III (residue), dilution 1 : 100.

Thus, the data obtained in the fractionation of irradiated heptane support and refine the data of Fig. 1.

The dependence of the absorption intensity in the region $\sim 38 \cdot 10^3$–$42 \cdot 10^3$ cm^{-1} on the molecular composition of alkanes is shown in Fig. 3a. On the abscissa is plotted the number of carbon atoms in various molecules of liquid alkanes, and on the ordinate the absorption values

$$E_{42} = \frac{D}{d} \times \text{dilution}$$

for the frequency $42 \cdot 10^3$ cm^{-1}

$\Big(D = \lg \frac{I_0}{I_{\text{trans}}}$; d is the layer thickness; the dilution of the irradiated product proved

Fig. 3

Figure 3: Fig. 3

necessary in order that the layer of substance should not absorb the entire beam of light) and S_i, which is the area bounded by the absorption curve, the ordinates corresponding to $38 \cdot 10^3$ and $44 \cdot 10^3$ cm^{-1}, and the abscissa axis, which is the line of complete transmission (the zero line of the initial, unirradiated alkane).

Both dependences, characterizing the absorption of dienes formed during the radiolysis of various alkanes, are represented by straight lines that approximate the experimental points well. Thus, within the range from C_6 to C_{12}, the absorption under consideration increases linearly with the increase in the number of CH_2 groups in the alkane molecules. Since the formation of dienes requires the removal of four hydrogen atoms, it may be concluded that the probability of such a reaction increases with the number of CH_2 groups.

Figure 3b presents the dependence of the intensity of absorption by irradiated heptane in the ultraviolet region on the irradiation dose. Although only three points have been determined, a straight line can be drawn through them with some confidence, since in this region up to $\sim 150 \cdot 10^6$ r all the quantities characterizing the change in heptane under the action of irradiation increase linearly.

but the points on the graph lie on a straight line without much scatter. Since, to a considerable extent, the absorption observed in the ultraviolet region under consideration in irradiated heptane occurs, as we saw above, at the expense of dienes (and polyenes), the straight line indicates a linear increase in the amount of dienes for doses from 40 to 150 million r. At smaller doses the dependence will almost certainly be linear. As for doses of $\sim 150 \cdot 10^6$ r, further experimental study is necessary in order to draw any definite conclusion.

The infrared absorption spectrum of the initial and irradiated (dose $158 \cdot 10^6$ r) heptane in the region $\sim$ 900–1000 cm^{-1} is shown in Fig. 4. The remaining regions of the infrared spectrum, recorded by us on an IKS-11 instrument, are not presented, since no changes in the spectrum were detected in them. The measurements were repeated twice with slits of 0.270 and 0.235 mm. As is evident from comparison of the curves in Fig. 4, irradiated heptane has a distinct absorption band with $\nu_{\max} \sim 965$ cm^{-1} (absent in the initial heptane). This band, as is known, corresponds to the bond $-CH = CH-$ in the trans position. It is obvious that although the formation of other olefins is possible during the radiolysis of heptane, the formation of trans-heptene is the most probable process. When this heptene is formed, a hydrogen molecule appears in the gas of the radiolysis products, i.e., this process is one of the dehydrogenation processes occurring during radiolysis. Similar results using infrared spectra were obtained in the work (^{2}).

Fig. 3. Dependence of absorption intensity on the molecular composition of

Fig. 4

Figure 4: Fig. 4

the irradiated hydrocarbon (**a**) and dependence of the absorption intensity of irradiated heptane on dose (**b**)

Fig. 4. Infrared absorption spectrum of initial (1) and irradiated ($158 \cdot 10^6$ r) (2) *n*-heptane

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