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Abstract

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REACTIVITY OF SATURATED HYDROCARBONS IN THEIR INTERACTION WITH FREE METHYL RADICALS IN THE LIQUID PHASE

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Free methyl radicals interact with hydrocarbon molecules according to the reaction:

$$\mathrm{RH} + \cdot\mathrm{CH_3} \xrightarrow{k^{\mathrm{H}}} \mathrm{R}\cdot + \mathrm{CH_4}.$$

To determine the relative magnitude of the constant k^{H}, in the present work a method was used based on comparison of the rate of the reaction under study with the rate of the reaction of the radical $\cdot\mathrm{CH_3}$ with a molecule of a standard compound containing a tritium label ($^{1-3}$).

If methyl radicals are generated in a mixture of the hydrocarbon under study, RH, and a standard, some fraction of which is labeled with tritium, then the composition of the methane formed may be expressed as follows:

$$\frac{[\mathrm{CH_4}]}{[\mathrm{CH_3T}]} = \frac{k^{\mathrm{H}}[\mathrm{RH}] + k^{\mathrm{H}}_{\mathrm{ct}}[\mathrm{RH_{ct}}]}{k^{\mathrm{T}}_{\mathrm{ct}}[\mathrm{RH_{ct}}]}. \tag{1}$$

Here $k^{\mathrm{H}}_{\mathrm{ct}}$ and $k^{\mathrm{T}}_{\mathrm{ct}}$ are the rate constants of the reaction of the radical $\cdot\mathrm{CH_3}$ with the hydrogen and tritium atoms of the standard hydrocarbon.

When methyl radicals are generated in a medium containing only the standard hydrocarbon, we have:

$$\frac{[\mathrm{CH_4}]}{[\mathrm{CH_3T}]} = \frac{k^{\mathrm{H}}_{\mathrm{ct}}[\mathrm{RH_{ct}}]}{k^{\mathrm{T}}_{\mathrm{ct}}[\mathrm{RT_{ct}}]}. \tag{2}$$

Expressing the concentrations of the tritium-containing compounds through their specific radioactivities and eliminating the constant $k^{\mathrm{T}}_{\mathrm{ct}}$ from (1) and (2), we obtain:

Fig. 1

Figure 1: Fig. 1

$$\frac{k^{\mathrm{H}}}{k^{\mathrm{H}}_{\mathrm{ct}}} = \frac{I^{0}_{\mathrm{M}} - I_{\mathrm{M}}}{I_{\mathrm{M}}} \frac{[\mathrm{RH}_{\mathrm{ct}}]}{[\mathrm{RH}]}, \tag{3}$$

where I^{0}_{M} is the activity of the methane obtained when methyl radicals are generated in the medium of the standard hydrocarbon, and I_{M} is that in the medium of a mixture of the standard and the hydrocarbon under study.

In deriving formula (3), it was assumed that the ratio $k^{\mathrm{H}}_{\mathrm{ct}}/k^{\mathrm{T}}_{\mathrm{ct}}$ does not change depending on the composition of the medium and is the same both for the pure substance $\mathrm{RH}_{\mathrm{ct}}$ and for its mixtures with the hydrocarbon under study. To verify the correctness of this assumption, a series of experiments was carried out with mixtures of cyclohexane and heptane, each of them in turn playing the role of the standard and of the substance under study. The heptane used as the standard hydrocarbon contained a tritium label in the 4-position.

Generation of methyl radicals was carried out by thermal decomposition of acetyl peroxide (∼ 0.05 mol/l) in the temperature range 55-90° C (±0.05°). The reaction was conducted in evacuated ampoules. After the reaction had been carried out, the ampoule was opened, and the methane was introduced into an internal counting counter-

···its filling and its radioactivity was determined. In the same counter the radioactivity of the hydrocarbons labeled with tritium was determined.

Figure 1 gives the experimental results in the coordinates ($k^{\mathrm{H}}_{\mathrm{RH}}/k^{\mathrm{H}}$) and $1/T$. As is seen from Fig. 1, the points obtained using both cyclohexane and heptane as the standard substance fall well on one and the same straight line. This indicates that the value $k^{\mathrm{H}}/k^{\mathrm{T}}$ for saturated hydrocarbons does not depend on the composition of the medium. Experiments carried out

Fig. 1. Dependence of $\lg(k^{\mathrm{H}}/k^{\mathrm{H}})$ on $1/T$. Crosses mark points obtained using cyclohexane-*t* as the standard; circles, heptane-^{14}t. In this and the following figures, the rate constant placed above the line (the hydrocarbon under study) is referred to the molecule as a whole; the one placed below the line (the standard hydrocarbon), to one C—H bond, under the assumption that all reactive bonds are equivalent. For heptane the number of bonds was taken as 10.5 (2). Each point in all figures is the average result of 2-3 measurements.

at the same temperature of 80°, but with cyclohexane—heptane mixtures of different composition, showed that the results do not depend on the choice of the standard substance and are practically independent of composition.

Further experiments were carried out with cis- and trans-decalins. In order to obtain more reliable results, two series of measurements were made, using as the standard substance in one case cyclohexane and in the other heptane. Values were obtained for the following ratios of constants: $k^{\mathrm{H}}/k^{\mathrm{H}}$, $k^{\mathrm{H}}\ /k^{\mathrm{H}}$, $k^{\mathrm{H}}/k^{\mathrm{H}}$, $k^{\mathrm{H}}\ /k^{\mathrm{H}}$. Since the ratio $k^{\mathrm{H}}/k^{\mathrm{H}}$ is known to us, by multiplying $k^{\mathrm{H}}/k^{\mathrm{H}}$ and $k^{\mathrm{H}}\ /k^{\mathrm{H}}$ by it we obtain, by an independent route, the values of $k^{\mathrm{H}}/k^{\mathrm{H}}$ and $k^{\mathrm{H}}\ /k^{\mathrm{H}}$. These values agreed well in both series of experiments, which convincingly indicates the reliability of the results obtained.

Experiments with variable composition of the decalin—standard hydrocarbon mixture showed that the rate constant of the reaction of cis-decalin with methyl radicals depends noticeably on the composition, as is seen from Fig. 2. An especially strong dependence is observed when heptane is used as the second component. Taking this circumstance into account, for finding the constants we used the results of experiments carried out with mixtures containing no more than 30 mole % cis- or trans-decalin.

Table 1

Hydrocarbon	Standard	$A^{\mathrm{H}}_{\mathrm{RH}}/A^{\mathrm{H}}$	$E^{\mathrm{H}} - E^{\mathrm{H}}_{\mathrm{RH}}$, kcal/mole	$k^{\mathrm{H}}_{\mathrm{RH}}/k^{\mathrm{H}}$ at 0°	$k^{\mathrm{H}}_{\mathrm{RH}}/k^{\mathrm{H}}$ at 80°	$k^{\mathrm{H}}_{\mathrm{RH}}/k^{\mathrm{H}}$ at 150°
Trans-decalin	Cyclohexane	$(2.1 \pm 0.4) \cdot 10^{-3}$	4540 ± 100	8.4	1.35	0.45
Trans-decalin*	»	$2.0 \cdot 10^{-3}$	4630			
Cis-decalin	»	$(2.4 \pm 0.3) \cdot 10^{-2}$	3200 ± 100	7.7	2.33	1.05
Cis-decalin*	»	$2.2 \cdot 10^{-2}$	3430			
Heptane	»	0.22 ± 0.04	1130 ± 130	1.75	1.1	0.43
Cyclopentane	»	16	−1600	0.86	1.65	2.4
Trans-decalin	Heptane	$(0.9 \pm 0.3) \cdot 10^{-2}$	3500 ± 250		1.38	
Cis-decalin	»	0.1 ± 0.04	2300 ± 300		2.63	

Note. The values of the constants and the corresponding Arrhenius parameters are referred to one C—H bond under the assumption that, for the hydrocarbons studied, all bonds have the same reactivity. For *n*-heptane, 10.5 reactive bonds were assumed (2). The data for cyclopentane are taken from work (1). Values marked with an asterisk (*) were obtained by calculation on the basis of constants measured relative to heptane.

Table 1 gives the values of the ratios of the rate constants for abstraction by methyl radicals of hydrogen atoms in the molecules of cis- and trans-decalins, *n*-heptane, and cyclopentane relative to the rate constant for abstraction of hydrogen atoms in cyclohexane and heptane molecules. As can be seen from these data, the averaged rate constants, calculated per bond at 80°, are fairly close to one another. At the same time, these constants have very strongly differing activation energies and, consequently, pre-exponential factors. As a result, at other temperatures the ratio of the reactivities of the same hydrocarbons will be substantially different, as is demonstrated by the data in the table.

Fig. 2. Dependence of the relative value of the rate constants on the composition of decalins with standard hydrocarbons. $RH_{\mathrm{st}} = C_6H_{12}$ or n-C_7H_{16}; 1 – for cis-decalin, 2 –for trans-decalin

Analysis of the values of the constants does not make it possible to outline an unambiguous relationship between the reactivity of a hydrocarbon and its structure over a considerable temperature interval. The reason for this is that the reactivity of compounds in liquid-phase free-radical reactions is determined not only by their structure and by the energy of the bonds participating in the reactions, but also by the structure and properties of the medium in which the reaction takes place.

One of the features of reactions occurring in condensed media is the so-called compensation effect. This effect has been traced in numerous examples of mono- and bimolecular reactions, heterogeneous reactions, and also in a number of physical processes ([4]). Formally it reduces to the fact that, for a number of related processes, the change in the constants characterizing the rates occurs in such a way that, with increasing activation energy, a simultaneous increase in the pre-exponential factor is observed. A number of attempts have been made to give a theory of this phenomenon as applied to chemical reactions ([5,6]). From the data of Table 1 it is evident that, in the cases studied by us, the compensation effect is also observed.

Fig. 3. Dependence of $\lg\left(k^H_{\mathrm{dec}}/k^H_{\mathrm{c}}\right)$ and $\lg\left(k^H_{\mathrm{dec}}/k^H_{\mathrm{h}}\right)$ on $1/T$. 1 –for cis-decalin, 2 –for trans-decalin

The broad occurrence of the compensation effect allowed S. Z. Roginskii and Yu. L. Khait to put forward the supposition that it is based on more general regularities than those on which the previous hypotheses were built ([4,7]). To explain the origin of the compensation effect, these authors considered a general model of the excitation process and, applying a statistical method of calculation, obtained an equation consistent with the experimental dependences. The essence of this explanation is that the probability of the activation process depends not on the average temperature of the system, but on the local temperature in a small region adjoining the reacting particles. The magnitude of this temperature, in turn, depends on E, which leads to the emergence of the compensation effect.

Such an explanation of the compensation effect presupposes a close connection between the activation process and the properties of the medium. This conclusion is confirmed by the dependence we have established of the values of the rate constants on the composition of the medium. As we have seen, this dependence is manifested especially strongly in the case of systems containing cis-decalin, which, in comparison with trans-decalin, is thermodynamically less stable. Owing to this instability, the bonds in the cis-decalin molecule differ from the bonds of trans-decalin and of other saturated hydrocarbons having unstrained structures. If it is assumed that the activation process of the reacting particles depends on the character of the interatomic bonds of the molecules of the medium, then the indicated dependence of the constants on composition becomes understandable. It follows from this that, in the general case, when two substances possessing bonds of different character react in one system, one should, as a rule, expect the relative reactivity to depend on the composition of the mixture.

The effect of the medium may be of interest from the point of view of controlling free-radical reactions. If competing reactions of two substances with one and the same radical occur in a system, then, by adding a third substance which does not react with the free radicals but influences the activation process in a definite way, it is possible to cause one reaction to be accelerated in comparison with the other. The effects noted in the present work are, from this point of view, too small. However, in a number of cases studied previously using systems containing aromatic compounds as an example, the effect of the medium on the relative reactivity of molecules in radical reactions was manifested considerably more distinctly (8).

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