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Abstract

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The Influence of Structure and Medium on the Reactivity of Hydrocarbons in Their Interaction with Free Methyl Radicals in the Liquid Phase

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The reactivity of hydrocarbons in the reaction with free methyl radicals can be characterized by the overall rate constant k_σ^H:

$$\mathrm{RH} + \cdot\mathrm{CH_3} \xrightarrow{k_\sigma^H} \mathrm{CH_4} + \mathrm{R}\cdot\,. \tag{1}$$

Similarly, to each type of C–H bond in the hydrocarbon molecule there may be assigned a partial rate constant k_i^H. Between the overall and partial constants there is the following relation:

$$k_\sigma^H = \sum_{i=1}^{i=r} n_i k_i^H,$$

where r is the number of types of C–H bonds, and n is the number of bonds of a given type. To a given type we assign structurally equivalent bonds, assuming that, to a known approximation, they are also equivalent in reactivity. A series of new data on the reactivity of hydrocarbons in the liquid-phase reaction with free methyl radicals was obtained by us by the method of competing reactions, using a tritium-labeled standard component. As the standard, n-heptane-4t was used. Reaction (1) was carried out in mixtures of tritiated heptane with the hydrocarbon under study, the source of free methyl radicals being the thermal decomposition of acetyl peroxide in the temperature range 60–90° (±0.05°). The rate constants of interest to us are related to the activity of the methane formed by the relation ([1]):

$$\frac{k_\sigma^H}{k^H} = 10.5\,\frac{I_0 - I}{I}\,\frac{[\mathrm{C_7H_{16}}]}{[\mathrm{RH}]}. \tag{2}$$

The constant k^H is referred to one secondary bond of the n-heptane molecule. Since the primary bonds of this hydrocarbon also participate in the reaction, the stoichiometric factor, equal to the number of secondary bonds, is increased

to 10.5 ([2]). I_0 and I are the specific molar activities of methane formed in the reaction with heptane-t alone and with its mixture with RH.

Figure 1 shows the dependence of k_σ^H/k^H for some hydrocarbons investigated by us on the composition of their mixtures with n-heptane at 80°. The use of labeled heptane in experiments with benzene did not provide the required accuracy of measurements (see the open circles in Fig. 1). Therefore the experiments were repeated using solutions of benzene-t in nonradioactive heptane, which made it possible to obtain the value of k^H/k^H with greater accuracy (black points in Fig. 1). In this case the calculation was carried out according to a formula analogous to (2):

$$\frac{k_\sigma^H}{k^H} = \frac{10.5\,I}{(I_0 - I)} \frac{[\mathrm{C_7H_{16}}]}{[\mathrm{C_6H_6}]}.$$

Here I_0 is the activity of the methane obtained in the decomposition of acetyl peroxide in a benzene-t medium.

It is seen from Fig. 1 that, as a rule, $k_\sigma^H/k_{\mathrm{GP}}^H$ has a linear dependence on the composition of the medium. Therefore, in order to compare reactivity, one should use the values of the constants obtained by extrapolation

Table 1

Hydrocarbon	$k_\sigma^H/k_{\mathrm{GP}}^H$ at $[C_7H_{16}] = 100\%$	$k_\sigma^H/k_{\mathrm{GP}}^H$ at $[RH] = 100\%$	$\frac{(k_\sigma^H/k_{\mathrm{GP}}^H)_{RH}}{(k_\sigma^H/k_{\mathrm{GP}}^H)_{\mathrm{GP}}} \cdot 100$
Cyclohexane	10.7 ± 0.3	11.2	104.5
Methylcyclohexane	18.8 ± 1	16.6	88.4
Methylcyclopentane	25.4 ± 2	23.0	90.6
trans-Decalin	27.5 ± 1	21.0	76.4
cis-Decalin	50.0 ± 1.5	30.0	60.0
Cyclohexene	144 ± 6	124	86.1
Cetylcyclopentene	168 ± 5	107	63.7
Isooctane (2,2,4-trimethylpentane)	1.6 ± 0.1	4.2	262
Benzene	0.4 ± 0.05	0.61	152
Cyclohexadiene-1,3	380 ± 20		
Cyclopentane	14.2 ± 0.2		

Note. For the hydrocarbons placed below the line, the values of $k_\sigma^H/k_{\mathrm{GP}}^H$ were obtained at their concentrations equal to 25–50 mol. % in the standard hydrocarbon. For cyclopentane the value of $k_\sigma^H/k_{\mathrm{GP}}^H$ was obtained by recalculating the value $k_\sigma^H/k_{\mathrm{CG}}^H$ (CG—cyclohexane) ([3]).

to zero concentration of the hydrocarbons under study. Table 1 gives the values of k_σ^H/k_{GP}^H; it also shows the increase (in percent) of these quantities when the concentration of the hydrocarbon under study is changed from 0 to 100%.

Analysis of the data in Table 1 shows that k_σ^H/k_{GP}^H, as a rule, decreases with increasing concentration of the hydrocarbon under study. In most cases the dependence of k_σ^H/k_{GP}^H on composition is weak; however, for individual hydrocarbons (cis-decalin, methylcyclopentene, benzene, isooctane) it is manifested rather strongly. The effect of the medium is especially noticeable in the case of isooctane.

Table 2

Nature of bond	Hydrocarbon	k_σ^H/k_{GP}^H
Primary	Heptane	0.1
Primary	Toluene	3.7
Secondary, unconjugated	Heptane	1.0
Secondary, unconjugated	Cyclohexane	0.89
Secondary, unconjugated	Cyclopentane	1.42
Secondary, conjugated	Cyclohexene	35.1
Secondary, conjugated	Methylcyclopentene	38.5
Secondary, conjugated	Cyclohexadiene-1,3	95
Tertiary	Methylcyclohexane	9.6
Tertiary	Methylcyclopentane	13.7
Tertiary	trans-Decalin	6.65
Tertiary	cis-Decalin	17.9
Aromatic C—H bonds	Benzene	0.067
Aromatic C—H bonds	Toluene (para-C—H bonds)	0.068

Table 2 gives the values of the partial rate constants at 80° for individual types of C—H bonds, referred to the rate constant of the secondary···

of the bond in *n*-heptane and those calculated from the data of Table 1 and of papers ([1],[2],[4]). In the calculation it was assumed that the following C—H bonds belong to the same type: primary ones: (a) in heptane, methylcyclohexane, and methylcyclopentane; (b) in toluene and methylcyclopentene; secondary unconjugated ones: (a) in cyclohexane and cyclohexene; (b) in cyclopentane and methylcyclopentene.

Fig. 1

Figure 1: Fig. 1

Our results are in qualitative agreement with the data of papers ([5],[6]), in which the reactivity of hydrocarbons in reaction with the tert-butoxy radical was studied. There are, however, a number of substantial discrepancies, apparently associated both with kinetic differences between methyl and tert-butoxy radicals and with differences in the experimental temperatures. Better agreement is observed with the results obtained in the papers of Schwarz and co-workers, in which reactions of methyl radicals were studied ([7]-[10]).

Fig. 1. Dependence of the reactivity (k_σ^H/k^H) of hydrocarbons on their concentration in *n*-heptane: 1 —methylcyclopentene-1; 2 —cyclohexene; 3 —methylcyclopentane; 4 —methylcyclohexane; 5 —2,2,4-trimethylpentane (isooctane); 6 —benzene (the tritiated *n*-heptane is indicated by white points; the benzene is indicated by black points).

The data of Table 2 make it possible to trace the influence of the principal structural factors on the reactivity of different hydrogen atoms. Conjugation of the C—H bond with a phenyl group or a double bond has an especially strong influence on reactivity. It is interesting that, in this respect, the influence of both the phenyl nucleus and the double bond is approximately the same. Indeed, from a comparison of heptane and toluene we find that replacement of an aliphatic radical by phenyl leads to an increase in reactivity by a factor of 37. Comparing cyclohexane with cyclohexene, and cyclopentane with methylcyclopentene, we find that introduction of a double bond into the ring leads to an increase in the reactivity of the α-C—H bond by a factor of 39-27.

Analysis of the results of papers ([7],[9],[10]) shows that, in liquid-phase reactions of methyl radicals with hydrocarbons, the increase in the reactivity of C—H bonds when they are conjugated is consistent with our data. In the case of toluene the reactivity increases by a factor of 39 (65°). In the case of propylene and butylenes the reactivity of conjugated bonds is 16-34 times higher than that of analogous unconjugated bonds (at 65°). In the case of double conjugation an additional increase in reactivity is observed. It is interesting that the value of the relative constant obtained by us for cyclohexadiene-1,3 (95; see Table 2) is very close to the analogous constant for pentadiene-1,4, in the molecule of which there is likewise double σ,π-conjugation, but no conjugation of the π-bonds with one another. The value calculated from the data of ([10]), k_σ^H/k^H, for pentadiene-1,4 is 84 at 65°.

Hydrogen atoms at primary, secondary, and tertiary carbon atoms differ rather strongly in their reactivity. A calculation based on the data given in Steacie' s monograph ([11]) shows that in the gas-phase reaction of methyl radicals at 80° the following ratio of constants is obtained:

$$k^H_{\text{prim}} : k^H_{\text{sec}} : k^H_{\text{tert}} = 0.1 : 1 : 10.$$

This ratio changes somewhat at high temperatures ([12]).

In our case, if the values of k^H_i/k^H_{gp} for tertiary C–H bonds are averaged, we obtain a ratio of constants very close to the gas-phase one:

$$k^H_{\text{prim}} : k^H_{\text{sec}} : k^H_{\text{tert}} = 1.0 : 1 : 12.$$

The conformation of the hydrocarbon molecule also affects its reactivity. In the compounds we studied, this influence is small and is reduced mainly, apparently, to the difference in reactivity of hydrogen atoms having a cis or trans arrangement relative to neighboring hydrogen atoms. The example of cyclopentane shows that in the case of a cis arrangement the reactivity increases by a factor of 1.6 compared with hydrogen atoms in the cyclohexane molecule. Approximately by the same factor the reactivity of tertiary hydrogen atoms in cis-decalin and methylcyclopentane increases in comparison with the tertiary hydrogen atom in methylcyclohexane (by factors of 1.85 and 1.43).

The question of the influence of the medium in free-radical reactions of nonpolar components has a relatively short history. Several works are known ([1,13]) in which such an influence was recorded and attempts were made to explain it. Our data make it possible to outline yet another approach to understanding this phenomenon. In the cases we studied, the influence of the medium is manifested most clearly in the isooctane–heptane system. As the concentration of isooctane tends to zero, its reactivity becomes equal to the reactivity of 15 primary hydrogen atoms ($k^H_e/k^H_{\text{gp}} = 1.6$ instead of the expected 1.5). The impression is created that under these conditions the tertiary and two secondary hydrogen atoms practically do not interact with methyl radicals.

A possible explanation of this fact may be the assumption that the isooctane molecule then exists in such a conformation in which the reactive bonds are completely shielded by methyl groups. As the concentration of isooctane increases, the conditions of close packing of the solution molecules change, and in this connection such conformations may appear in which the shielding effect disappears or is weakened. In the same way one can explain the influence of composition in the case of cis- and trans-decalins, the molecules of which possess a set of different conformations. It is evident, however, that a number of other effects also exist, since from the standpoint of conformational changes alone it is impossible to explain the influence of composition, for example, in the case of benzene.

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