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V. L. Antonovskii, I. V. Berezin, and L. V. Shevelkova

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Abstract

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Relative Reactivity of C–H and C–T Bonds of *n*-Heptane, Benzene, Toluene, Ethylbenzene, and Cyclohexane in Reaction with $CH_3\cdot$ in the Liquid Phase

Influence of the Phenyl Group and of the Aromaticity of the Medium

(Presented by Academician N. N. Semenov, April 27, 1960)

To determine the relative reactivity, a method was used in which individual CH bonds were labeled with tritium. Let us consider a system consisting of two organic compounds, one of which, A, has r types of reactive CH bonds and is labeled with tritium by partial replacement of hydrogen atoms in bonds of the j-th type, while the other, B, is unlabeled and has p types of CH bonds.

If free methyl radicals are generated in this system, then the composition of the methane formed in the reaction

$$RH(T) + CH_3\cdot \rightarrow R\cdot + CH_4(CH_3T) \quad (RH = A \text{ or } B)$$

is expressed by the following relation:

$$\frac{[CH_4]}{[CH_3T]} = \frac{[A]\sum^r n_i k_i^H + [B]\sum^p n_i k_i^H}{k_{jA}^T[A-t]}, \tag{1}$$

where k_{jA}^T is the rate constant of the reaction of $CH_3\cdot$ with the tritium atom of the j-bond in substance A; k_i^H is the rate constant of the same reaction with the various bonds of substances A and B; n is the number of bonds of one type; the square brackets denote the concentrations of the corresponding compounds. Expressing the concentrations of tritiated compounds in terms of their specific activities, we obtain:

$$\frac{I_A}{I_M} = \frac{k_{\sigma A}^H}{k_{jA}^T} + \frac{k_{\sigma B}^H}{k_{jA}^T}\cdot\frac{[B]}{[A]}, \tag{2}$$

where

$$k_{\sigma A}^H = \sum^r n_i k_i^H; \quad k_{\sigma B}^H = \sum^p n_i k_i^H;$$

I_A is the specific activity of substance A; I_M is that of methane.

In accordance with (2), ratios of various rate constants can be found experimentally.

a) **Determination of $k_{\sigma A}^H/k_{jA}^T$.** For this purpose, $CH_3\cdot$ is generated in A without an admixture of B (the second term on the right-hand side of (2) is equal to zero).

b) **Determination of** $k^{\mathrm{H}}_{\sigma B}/k^{\mathrm{H}}_{\sigma A}$. Methyl radicals are generated in a mixture of A and B. The desired ratio is found from the equation

$$k^{\mathrm{H}}_{\sigma B}/k^{\mathrm{H}}_{\sigma A} = [A]/[B] \times (I^0_M/I_M - 1),$$

where I^0_M is the activity of methane determined in a). As can be seen, determination of I_A is unnecessary in this case.

c) **Determination of** $k^{\mathrm{H}}_{\sigma B}/k^{\mathrm{T}}_{jA}$. If the specific radioactivity of A is high, then, taking $[A] \ll [B]$, determining I_M and I_A, and neglecting the first term on the right-hand side of (2), one finds $k^{\mathrm{H}}_{\sigma B}/k^{\mathrm{T}}_{jA}$.

According to the scheme considered, we determined the rate constants for abstraction by the methyl radical of hydrogen atoms (k^{H}) from *n*-heptane (secondary bonds–

namely, benzene and toluene (unlabeled), relative to the rate constant for cyclohexane, which was taken as the "standard" hydrocarbon and was labeled with tritium. In another series of experiments, the rate constants for abstraction of a tritium atom by the same radical from the methyl groups of toluene and ethylbenzene were determined relative to the constant for abstraction of a hydrogen atom in cyclohexane, which made it possible to trace the influence of the phenyl group on the reactivity of the corresponding bonds.

The source of $CH_3\cdot$ was the thermal decomposition (55—85° ± 0.05°) of acetyl peroxide at concentrations of 0.02—0.03 *M* ([1]). The reaction was carried out in evacuated ampoules; methane was separated from the other components of the mixture, and its activity was determined in an internal-filling counter. The activity of the hydrocarbons was determined in the same counter. Details of the procedure have been described previously ([2, 3]). In *n*-heptane, the rate constant for abstraction of primary hydrogen atoms by a methyl radical at 55—85° is approximately 12 times smaller than the rate of abstraction of secondary atoms ([2]). Therefore $k^{\mathrm{H}}_{\mathrm{g}} = 10.5\, k^{\mathrm{H}}_{\mathrm{sec,g}}$, i.e., $n = 10.5$. For toluene $n = 3$, since the C-H bonds of the methyl group are approximately 150 times more reactive than the C-H bonds of the ring ([4]). In cyclohexane we considered all C-H bonds structurally equivalent and assumed $n = 12$.

(Figure: Fig. 1. Dependence of $k^{\mathrm{H}}_{63}/k^{\mathrm{H}}_{\mathrm{cg}}$ on composition (mol.%): a–55°; b–85°)

Fig. 1. Dependence of $k^{\mathrm{H}}_{63}/k^{\mathrm{H}}_{\mathrm{cg}}$ on composition (mol.%): *a*—55°; *b*—85°.

Table 1 gives the results of experiments with *n*-heptane. The extent of decomposition of acetyl peroxide was 50% throughout, since it had been shown that differences in the extent do not affect the results ([5]). Each value in Table 1 was obtained as the result of at least two measurements.

Experiments with different values of $[C_6H_{12}]/[C_7H_{16}]$ show that, for saturated hydrocarbons, the ratio of the rate constants does not depend on composition within the limits of error. The temperature dependence of the ratios of the constants has the following form:

$$\frac{k^{\mathrm{H}}_{\mathrm{sec,g}}}{k^{\mathrm{H}}_{\mathrm{cg}}} = 10 \exp\left(-\frac{1440 \pm 300}{RT}\right).$$

Attention is drawn to the small magnitude of the preexponent $k^{\mathrm{H}}_{\mathrm{cg}}$ in comparison with $k^{\mathrm{H}}_{\mathrm{sec,g}}$. It is possible that this is connected with the high symmetry of cyclohexane. Indeed:

$$A^{\mathrm{H}}_{\mathrm{g}}/A^{\mathrm{H}}_{\mathrm{cg}} \sim \sigma_{\mathrm{cg}}/\sigma_{\mathrm{g}},$$

where A are the corresponding preexponents, and σ are the symmetry numbers. For cyclohexane $\sigma = 6$, and for n-heptane $\sigma = 1$.

Table 1

T, °C	$k^{\mathrm{H}}_{\mathrm{sec,g}}/k^{\mathrm{H}}_{\mathrm{cg}}$ at $[C_6H_{12}]/[C_7H_{16}] = 1.4$	$k^{\mathrm{H}}_{\mathrm{sec,g}}/k^{\mathrm{H}}_{\mathrm{cg}}$ at $[C_6H_{12}]/[C_7H_{16}] = 1.097$	$k^{\mathrm{H}}_{\mathrm{sec,g}}/k^{\mathrm{H}}_{\mathrm{cg}}$ at $[C_6H_{12}]/[C_7H_{16}] = 0.0655$
85	1.49 ± 0.15	1.43 ± 0.1	1.32 ± 0.05
55	1.27 ± 0.13	1.05 ± 0.08	

Experiments with benzene–cyclohexane and toluene–cyclohexane mixtures (cyclohexane labeled) showed that the determined values of the ratios of rate constants depend strongly on the composition of the mixtures used in the experiments (see Figs. 1 and 2). The effect of the concentration of the aromatic hydrocarbon on the value of the ratio of constants has the same character for both benzene and toluene. In both cases the ratios of the constants decrease with increasing concentration of the aromatic hydrocarbon. After certain concentrations have been reached, the ratios change–

proceed considerably more slowly, tending thereby toward the values characteristic of the same reactions in the gas phase (at 85° $k^{\mathrm{H}}_{\mathrm{bz}}/k^{\mathrm{H}}_{\mathrm{cg}} = 0.07$; $k^{\mathrm{H}}_{\mathrm{tl}}/k^{\mathrm{H}}_{\mathrm{cg}} = 2.2$ ([6])).

A similar effect of aromatic compounds on the reactivity of chlorine atoms in the reaction with saturated hydrocarbons was found by G. Russell ([7]). He explained this phenomenon by the formation of π-solvates of chlorine atoms, which thereby become less active. In our case the matter is apparently considerably more complex. If one proceeds only from the idea of π-solvates of toluene or benzene with the methyl radical, then one should expect an increase in the selectivity of its action and an increase in the ratio $k^{\mathrm{H}}_{\mathrm{tl}}/k^{\mathrm{H}}_{\mathrm{cg}}$ with increasing toluene concentration, which, however, is not observed.

The observed influence of the medium on the ratio of the rate constants of elementary reactions compelled us to change the order of work in experiments studying the influence of the phenyl group on the reactivity of primary bonds.

For this purpose highly radioactive toluene and ethylbenzene containing a tritium atom in the CH_3 group were synthesized. The experiments were carried out with small additions of toluene and ethylbenzene to cyclohexane. The calculation was performed from equation (2) according to ([8]). The results are presented in Table 2.

(Figure: Figure 2)

Fig. 2. Dependence of $k_{\text{tl}}^{\text{H}}/k_{\text{cg}}^{\text{H}}$ on composition (mol. %): *a*–55°; *b*–85°

The differences in activation energies and the ratios of pre-exponential factors calculated from the data of Table 2 are given in Table 3. Analysis of the results obtained shows that, in the region of low concentrations of aromatic compounds, the value of the relative rate constant for abstraction of a tritium atom from the methyl group is practically independent of composition both for toluene and for ethylbenzene. Therefore the values obtained may be regarded as "true," not distorted by that peculiar influence exerted by aromatic compounds at higher concentrations.

Table 2

Temp., °C	$k_{\text{cg}}^{\text{T}}/k_{\text{cg}}^{\text{H}}$ at hydrocarbon concentration in C_6H_{12}, wt.%}			
	0.134	0.200	0.466	4.00
Toluene				
85	0.190 ± 0.002	0.205 ± 0.003	0.166 ± 0.002	0.170 ± 0.002
70	0.180 ± 0.002	–	0.152 ± 0.003	0.154 ± 0.002
55	0.172 ± 0.002	0.174 ± 0.002	0.135 ± 0.005	0.142 ± 0.002
Ethylbenzene				
	0.140	0.337	0.644	
85	0.083 ± 0.002	0.105 ± 0.002	0.100 ± 0.001	–
55	0.155 ± 0.002	0.158 ± 0.002	–	–

For toluene, discarding the values of $A_{\text{tl}}^{T}/A_{\text{cg}}^{H}$ and ΔE for the concentration 0.134% as clearly anomalous, we have $k_{\text{tl}}^{T}/k_{\text{cg}}^{H} = 1.4\exp(-1400/RT)$. If the magnitude of the isotope effect for toluene in our case is taken to be $0.55\exp(2200/RT)$ ([5]), then at 85° we have $k_{\text{tl}}^{H}/k_{\text{cg}}^{H} = 2.3$, which is close to the value obtained by Steacie for the gas phase ([6]). The obtained value of $k_{\text{tl}}^{H}/k_{\text{cg}}^{H}$ is somewhat lower than would be expected on the basis of the Polanyi relation ([8]). Evidently, this is connected with conjugation of the unpaired electron introduced into the activated complex by the $CH_3\cdot$ radical with the aromatic

system of bonds of toluene, which should cause an additional increase in the energy barrier of the reaction.

Table 3

Concentration in C_6H_{12}, wt. %	A^T/A^H_{cg}	$\Delta E = E^T - E^H_{cg}$, kcal/mol
Toluene	**Toluene**	**Toluene**
0.134	0.6	0.8 ± 0.2
0.200	1.3	1.3 ± 0.25
0.466	1.6	1.6 ± 0.4
4.00	1.2	1.4 ± 0.2
Ethylbenzene	**Ethylbenzene**	**Ethylbenzene**
0.140	10^{-4}	-4.8 ± 0.3
0.337	$1.2 \cdot 10^{-3}$	-3.2 ± 0.3

Comparison of the reactivity of the CH_3 groups of toluene and ethylbenzene can be made only for C-T bonds. At 85°, on average $k^T_{tl} : k^T_{eb} = 1.9$, which indicates a relatively slow attenuation of the activating influence of the phenyl group with distance. A comparison with the reactivity of the C-T bond in the methyl group of *n*-heptane can be made on the basis of the data of ([2]) and of the present work. Finally, at 85° we have:

$$k^T_{hp} : k^T_{eb} : k^T_{tl} = 1 : 14.5 : 28.$$

We see that the phenyl group indeed exerts a strong labilizing effect on the hydrogen atoms in the CH_3 group of toluene. It is remarkable that this influence continues to manifest itself to a very strong degree also in the methyl group of ethylbenzene. In this connection it is appropriate to draw attention to the unusual values of the pre-exponential factor and of the activation energy for abstraction of a tritium atom in ethylbenzene. It is possible that the mobility of the primary hydrogen atoms of ethylbenzene is explained not by the electromeric effect of the aromatic nucleus, but by another effect, the mechanism of which is as yet unknown to us.

Moscow State University
named after M. V. Lomonosov

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