Kinetic Isotope Effects of Tritium in the Liquid-Phase Reaction of Hydrocarbons with Free Methyl Radicals

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Kinetic Isotope Effects of Tritium in the Liquid-Phase Reaction of Hydrocarbons with Free Methyl Radicals

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The study of the kinetic isotope effects of tritium, and of the regularities of their variation depending on the structure of the reacting particles, the medium, temperature, etc., is a problem of great importance. The solution of these questions not only creates a basis for quantitative comparisons in investigations of the chemistry and kinetics of elementary processes, but also makes it possible in a number of cases to draw conclusions about the character of the activated states through which the reaction proceeds (^{1,2}).

We have determined intermolecular kinetic isotope effects of tritium in reactions of hydrocarbons with free methyl radicals ($i = k^H/k^T$):

$$\mathrm{RH} + \mathrm{CH_3^{\cdot}} \xrightarrow{k^H} \mathrm{R\cdot} + \mathrm{CH_4}, \tag{I}$$

$$\mathrm{RT} + \mathrm{CH_3^{\cdot}} \xrightarrow{k^T} \mathrm{R\cdot} + \mathrm{CH_3T}. \tag{II}$$

Determination of the value of the kinetic isotope effect when a small fraction of hydrogen atoms is replaced by tritium is possible in the case where the molecule of the hydrocarbon under investigation contains only one type of reactive bond. Then:

$$\frac{[\mathrm{CH_4}]}{[\mathrm{CH_3T}]} = \frac{nk^H[\mathrm{RH}]}{k^T[\mathrm{RT}]}.$$

Here n is the number of reactive C–H bonds in the RH molecule. If $[\mathrm{RT}] \ll [\mathrm{RH}]$, then $\gamma I_{\mathrm{RH}} = [\mathrm{RT}]/[\mathrm{RH}]$, where I_{RH} is the specific activity of the compound, expressed as the number of pulses per unit time per mole, and γ is a proportionality coefficient that depends only on the construction of the counter used. Finally we obtain:

$$i = \frac{k^H}{k^T} = \frac{I_{\mathrm{RH}}}{nI_m}, \tag{1}$$

where I_m is the specific radioactivity of the methane formed in the experiment. The determinations were carried out with benzene and toluene. In view of the fact that the reactivity of the hydrogen atoms in the ring of toluene is 150-170 times less than in the methyl group (³), one may take $n = 3$ for it.

Determination of the isotope effect in the case of aromatic and unsaturated compounds requires special caution, since, alongside the principal substitution reaction, parallel reactions not taken into account by equation (1) may occur. In this connection it is appropriate to recall the ambiguity of the results of Vilen and Iliel (⁴) in determining the isotope effect for the same reaction with toluene deuterated in the CH_3 group. In the interaction of $CH_3\cdot$ with aromatic compounds, the source of methane, in addition to reactions

(I) and (II) may also involve the following process (using benzene as an example):

$$C_6H_6 + CH_3\cdot \to C_6H_6(CH_3)\cdot \xrightarrow{+CH_3\cdot} C_6H_5CH_3 + CH_4$$

The isotope effect of this reaction should be equal to 1, as was found by Price and Convery for the phenylation of 2,4-dinitrobenzene (⁵). If in our case (benzene, toluene with $CH_3\cdot$) this reaction plays an appreciable role, then the magnitude of the isotope effect calculated from equation (1) should depend on the concentration of methyl radicals.

As a source of methyl radicals we used acetyl peroxide, the decomposition of which was carried out in a medium of tritium-labeled hydrocarbons (²). The concentration of methyl radicals depends both on the extent of peroxide decomposition and on its initial concentration. Table 1 gives the results of experiments* with benzene-*t* at a temperature of 85°, from which it follows that the magnitude of the isotope effect depends neither on the initial concentration nor on the extent of decomposition of acetyl peroxide.

Table 1

$I^*_{C_6H_6}$	Initial peroxide conc., mol/l	I_{CH_4} at 10% decomposition	I_{CH_4} at 25% decomposition	I_{CH_4} at 50% decomposition	Average of 5 experiments	$i = \frac{k^H}{k^T}$
5960 ± 100	0.025	165 ± 4	165 ± 1	167 ± 1	166 ± 2	5.98 ± 0.13
5960 ± 100	0.010	163 ± 3	161 ± 2	164 ± 1	163 ± 2	6.09 ± 0.13

It follows from Table 1 that the experimental results are not distorted by interaction of the methyl radical with the reaction products. Experiments with toluene-αt lead to the same conclusions.

Table 2

Temp., °C	Benzene: $I_{C_6H_6}$	Benzene: I_{CH_4}	Benzene: k^H/k^T	Toluene: $I_{C_6H_5CH_3}$	Toluene: I_{CH_4}	Toluene: k^H/k^T
85	5960 ± 100	166 ± 1	5.98 ± 0.13			
85	5000 ± 80	136 ± 1	6.19 ± 0.13	35200 ± 700	968 ± 7	12.1 ± 0.1
85	5770 ± 30	163 ± 1.5	5.90 ± 0.06			
70	5770 ± 30	145 ± 2	6.63 ± 0.13	35200 ± 700	829 ± 11	14.14 ± 0.2
55	5770 ± 30	130.6 ± 2	7.36 ± 0.09	35200 ± 700	737 ± 6	15.9 ± 0.3

Table 2 shows the results of experiments with benzene and toluene carried out at temperatures of 55, 70, and 85° (±0.05°). The methane activity values were obtained from 3–6 experiments; the errors indicated throughout are root-mean-square errors.

The dependence of $\lg k^H/k^T$ on $1/T$ is linear. The values of the pre-exponential-factor ratios (A^H/A^T) and the activation-energy differences ($E^T - E^H$), calculated by the least-squares method, are given in Table 3. The values of these quantities for other hydrocarbons are also given there ([6],[7]).

For the secondary bonds of *n*-heptane, cycloheptane, and cyclopentane, despite the considerable structural peculiarity of the latter (ring strain, cis arrangement of all hydrogen atoms), the isotope effect is practically the same both in ΔE and in the ratio of the pre-exponential factors. On this basis one may conclude that, for all secondary aliphatic, unconjugated carbon-hydrogen bonds, the kinetic isotope effect of tritium

Table 3

Hydrocarbon	A^H/A^T	$\Delta E = E^T - E^H$, kcal/mole	k^H/k^T at 85°
Benzene	0.66	1570 ± 100	6.0
Toluene	0.55	2200 ± 100	12.1
Cyclohexane	0.38	2700 ± 100	17.2
Cyclopentane	0.16	3500 ± 350	22.8
Cyclopentane	0.19	3430 ± 250	23.5

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* In Tables 1 and 2 the specific activity is expressed in imp/min per 1 mm pressure of substance in the count

Hydrocarbon	A^H/A^T	$\Delta E = E^T - E^H$, kcal/mole	k^H/k^T at 85°
n-Heptane (secondary bonds)	0.20	3400 ± 130	23.2

in reaction with free methyl radical is the same. Calculated from the available data, the expression for the averaged isotope effect for secondary bonds has the following form:

$$k^H/k^T = 0.18\exp(3450/RT).$$

A different picture is observed for the remaining hydrocarbons, for which the influence of structural factors is manifested more distinctly. In the case of cyclohexane, the change in the magnitude of the isotope effect is connected mainly with conformational features and with the presence of structural nonequivalence of the bonds. It is more correct in this case to speak of the isotope effect separately for axial and equatorial bonds. Experimentally, the mean isotope effect is measured,

$$i_{\text{cp}} = \frac{k_e^H + k_p^H}{k_e^T + k_p^T}$$

(the subscripts e and p correspond to equatorial and polar bonds). By simple transformations it can be shown that

$$1 + \frac{k_e^H}{k_p^H} = \frac{i_{\text{cp}}}{i_p}\left(1 + \frac{i_p}{i_e}\frac{k_e^H}{k_p^H}\right), \tag{2}$$

where i_p and i_e are the isotope effects for polar and equatorial bonds. From spectroscopic data for $C_6H_{11}D$ (^{8}) it follows that, energetically, polar and equatorial bonds are close. On this basis one may set $k_e^H/k_p^H \simeq 1$, in view of which (2) is rewritten as

$$\frac{1}{i_e} + \frac{1}{i_p} \simeq \frac{2}{i_{\text{cp}}}. \tag{3}$$

Equatorial C–H bonds are structurally close to ordinary secondary bonds of alicyclic hydrocarbons. If one assumes that $i_e = i_{\text{sec}} = 0.18\exp(3450/RT)$, then for i_p the following expression is obtained:

$$i_p = 0.48\exp(2300/RT).$$

The character of the change in the magnitudes of isotope effects in the toluene —n-heptane series (see Table 3) indicates a definite dependence of them on the energetics of the C—H bonds being broken. For reactions of hydrogen-atom abstraction by $CH_3\cdot$ radicals it is known (^{6,9}) that $E^H_{\text{cp}} - E^H_{\text{tl}} = 2.2$ kcal; $E^H_{\text{gp}} - E^H_{\text{tl}} = 2.0$ kcal; $E^H_{\text{cg}} - E^H_{\text{tl}} = 0.6$ kcal; (cp—cyclopentane; gp—n-heptane; cg—cyclohexane; tl—toluene). In other words, the activation energy decr-

decreases in the series: secondary CH bonds, cyclohexane, toluene. In the same direction both ΔE of the isotope effect and its magnitude decrease. The value A^H/A^T thereby increases. The magnitude of the isotope effect in benzene differs sharply, which apparently is connected with the influence of the aromatic ring on the energy levels of the transition state.

The magnitude of the kinetic isotope effect depends not only on the nature of the bond being broken, but also on the type of attacking particle. In the series $Cl\cdot$; $Br\cdot$; N-succinimidyl; $(CH_3)_3CO\cdot$, $CH_3\cdot$, the deuterium isotope effect increases (^{10}). Therefore, the values obtained in the present work may be regarded as the upper limit of the values of the kinetic isotope effects of tritium with other free-radical particles.

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