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Abstract

Full Text

PHYSICAL CHEMISTRY

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STUDY OF ELEMENTARY REACTIONS OF TRITIUM-ATOM ABSTRACTION FROM PENTATRIACONTANE-18*t* BY CYCLOHEXYL AND HEPTYL FREE RADICALS IN THE LIQUID PHASE

(Presented by Academician N. N. Semenov, 25 VII 1961)

The rate of free-radical substitution reactions

$$R\cdot + R_1H \rightarrow RH + R_1\cdot$$

is determined both by the properties of the molecule R_1H and by those of the radical R·. Recently, much attention has been devoted to establishing regularities relating the reactivity of stable molecules to their structure. These same questions are being developed much less for free radicals, especially in liquid-phase reactions. To a considerable extent this is connected with experimental difficulties.

In the present work a methodological procedure is considered that makes it possible to obtain the value of the ratio of the rate constant for the reaction of abstraction of a tritium atom in the molecule of an organic compound taken as standard by some free radical to the square root of the rate constant for recombination of these radicals. This ratio is an important characteristic of the reactivity of a free radical and makes it possible to estimate with good accuracy the activation energy of the elementary reaction. The ratios of constants obtained in the present work for cyclohexyl and heptyl free radicals also made it possible to establish a close analogy between elementary free-radical reactions in the liquid and gas phases.

Suppose that in a medium of compound RH, where R is any radical, the formation of free radicals R· occurs at a rate w_0. The disappearance of radicals may occur as a result of recombination or disproportionation, and under stationary conditions the rate of these reactions is equal to the rate of formation of free radicals:

$$2R\cdot \xrightarrow{k_p} R - R \text{ or } RH + R''H,$$

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Fig. 1

Figure 1: Fig. 1

where R″H is an olefin. Thus $w_0 = k_p[\mathrm{R}\cdot]^2$, so that

$$[\mathrm{R}\cdot] = w_0^{1/2} k_p^{-1/2}, \tag{1}$$

where k_p is the rate constant of the recombination reaction. If a small amount of a compound $\mathrm{R_1H}$, containing $\mathrm{R_1T}$ molecules, is added to this system, then formation of the compound RT will occur:

$$\mathrm{R}\cdot + \mathrm{R_1T} \xrightarrow{k^T} \mathrm{RT} + \mathrm{R_1}\cdot .$$

If the addition of $\mathrm{R_1H} + \mathrm{R_1T}$ is so small that it practically does not affect the composition of the free radicals in the system, then expression (1) remains valid for the concentration of radicals R·. Then the concentration of RT after a time Δt, taking (1) into account, will be equal to:

$$[\mathrm{RT}] = k^T[\mathrm{R}\cdot][\mathrm{R_1T}]\,\Delta t = k^T k_p^{-1/2} w_0^{1/2}[\mathrm{R_1T}]\,\Delta t. \tag{2}$$

Expressing the concentrations RT and $\mathrm{R_1T}$ through their specific activities (I) by formulas (1):

$$[\mathrm{RT}] = \frac{I_{\mathrm{RH}}[\mathrm{RH}]}{\gamma}; \qquad [\mathrm{R_1T}] = \frac{I_{\mathrm{R_1H}}[\mathrm{R_1H}]}{\gamma}$$

we obtain from (2):

$$\frac{I_{\mathrm{RH}}[\mathrm{RH}]}{I_{\mathrm{R_1H}}[\mathrm{R_1H}]\,\Delta t} = k^T k_p^{-1/2} w_0^{1/2}. \tag{3}$$

All quantities on the left-hand side of (3), as well as w_0, are accessible to direct determination.

Fig. 1. Dependence of

$$\frac{I_{\mathrm{RH}} \cdot [\mathrm{RH}]}{I_{\mathrm{PTK}} \cdot [\mathrm{PTK}] \cdot \Delta t} \cdot 10^8 \ \mathrm{sec}^{-1}$$

(on the ordinate axis) on $w_0^{1/2} \cdot 10^4 \ \mathrm{mole}^{1/2} \cdot l^{-1/2} \cdot \mathrm{sec}^{-1/2}$ (on the abscissa axis). **1** –for cyclohexyl radicals, **2** –for heptyl radicals.

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We investigated the systems $C_6H_{12} + C_6H_{11}\cdot$ and $C_7H_{16} + C_7H_{15}\cdot$, in which radical initiation was carried out by the reactions:

$$C_6H_{12} + CH_3\cdot \rightarrow C_6H_{11}\cdot + CH_4, \tag{4}$$

$$C_7H_{16} + CH_3\cdot \rightarrow C_7H_{15}\cdot + CH_4. \tag{5}$$

To obtain methyl radicals, the thermal decomposition of acetyl peroxide[2] was used at its concentrations in the hydrocarbon from $6.2\cdot10^{-3}$ to $6.2\cdot10^{-2}$ mole/l. To ensure constancy of the initiation rate, the degree of decomposition did not exceed 10%. In the heptyl radicals formed by reaction (5), the free valence may be located at any of the secondary carbon atoms with approximately equal probability[1]. Owing to the very high rates of reactions (4) and (5), the concentration of $CH_3\cdot$ in the system is very small and does not affect the termination of the radicals $C_6H_{11}\cdot$ and $C_7H_{15}\cdot$ that are formed.

The value w_0 was determined from the amount of methane formed. Pentatriacontane labeled with tritium in the 18th position was used as the substance R_1H (0.02% $C_{35}H_{71}T$), additions of which amounted to 1.5–1.7 mg/ml. At the same time, along with reactions (4) and (5), reactions occurred in the systems that led to exchange of tritium between pentatriacontane (PTK) and the corres-

corresponding hydrocarbon:

$$C_6H_{11}\cdot + C_{35}H_{71}T \xrightarrow{k^T} C_6H_{11}T + C_{35}H_{71}\cdot,$$

$$C_7H_{15}\cdot + C_{35}H_{71}T \xrightarrow{k^T} C_7H_{15}T + C_{35}H_{71}\cdot.$$

The concentration of the radicals $C_{35}H_{71}\cdot$ and $C_{35}H_{70}T\cdot$ formed in this process is approximately 500 times smaller than the concentration of cyclohexyl and heptyl radicals and has practically no effect on the rates of their disappearance.

The reaction was carried out in sealed and evacuated ampoules, which were placed in a thermostat (±0.05°C). After completion of the reaction, cyclohexane or heptane was separated from pentatriacontane by distillation, and their radioactivity was measured in an internal-filling counter. To determine the activity of pentatriacontane, it was subjected to combustion ([3]). The counter was a brass tube 35 mm in diameter and 520 mm long, with Teflon insulation of the leads and a platinum filament 0.1 mm thick. The counter plateau at a temperature of 69°C and a cyclohexane vapor pressure of 300 mm, without addition of any other gases, lies in the range 4000–4700 V and has a slope of 1% per 100 V.

Table 1

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Fig. 2. Dependence of $(k^T/k_p^{1/2})$ on $1/T$: 1 –for cyclohexyl radicals, 2 –for heptyl radicals

Figure 2: Fig. 2. Dependence of $(k^T/k_p^{1/2})$ on $1/T$: 1 –for cyclohexyl radicals, 2 –for heptyl radicals

T, °C	$k^T/k_p^{1/2} \cdot 10^5$, $\mathrm{l}^{1/2} \cdot \mathrm{mol}^{-1/2} \cdot \mathrm{sec}^{-1/2}$ – C_6H_{11}·	$k^T/k_p^{1/2} \cdot 10^5$, $\mathrm{l}^{1/2} \cdot \mathrm{mol}^{-1/2} \cdot \mathrm{sec}^{-1/2}$ – C_7H_{15}·
60	0.65	0.21
70	1.21	0.37
80	1.82	0.64
85	2.73	0.91

Figure 1 presents the experimental results. As can be seen, the quantity

$$\frac{I_{\mathrm{RH}}[\mathrm{RH}]}{I_{\mathrm{PTK}}[C_{35}H_{72}]\,\Delta t}$$

is directly proportional to $w_0^{1/2}$. This indicates that in both cases a quadratic disappearance of free radicals is observed. The tangents of the slopes of the straight lines give the desired values of the ratios of constants (see Table 1).

Fig. 2. Dependence of $(k^T/k_p^{1/2})$ on $1/T$: 1 –for cyclohexyl radicals, 2 –for heptyl radicals.

Figure 2 gives the corresponding semilogarithmic transformations, from which one obtains:

$$(k^T/k_p^{1/2}) = (1.0 \pm 0.1) \cdot 10^3 \times \exp(-12400 \pm 300)/RT\, \mathrm{l}^{1/2} \cdot \mathrm{mol}^{-1/2} \cdot \mathrm{sec}^{-1/2}, \quad (6)$$

$$(k^T/k_p^{1/2}) = (2.1 \pm 0.2) \cdot 10^3 \times \exp(-13700 \pm 300)/RT\, \mathrm{l}^{1/2} \cdot \mathrm{mol}^{-1/2} \cdot \mathrm{sec}^{-1/2}. \quad (7)$$

The activation energy of the recombination processes is small and practically the same for radicals of similar nature. This makes it possible to assume that the activation energies of the corresponding elementary reactions are equal to

$$E^T = 14000 \text{ cal/mol} \quad \text{and} \quad E^T = 13000 \text{ cal/mol}.$$

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Analysis of literature data ([4–12]) shows that, for analogous reactions in the gas phase of the radicals $CH_3\cdot$, $CF_3\cdot$, $C_2H_5\cdot$, iso-$C_3H_7\cdot$, n-$C_3H_7\cdot$, and n-$C_3H_7\cdot$ with molecules of the most varied structure, in 70% of cases the values of $A/A_p^{1/2}$ (A and A_p are the preexponential factors of the rate constants) lie within the range $0.5\cdot10^3$–$5\cdot10^3$ $\text{mol}^{-1/2}\cdot\text{l}^{-1/2}\cdot\text{sec}^{-1/2}$. As we see, the values of the preexponents of the rate constants of the reactions studied by us also fall within this range. This points to the well-known commonality of the regularities governing transport and collisions of reacting particles in both the gas and liquid phases.

In analyzing the activation-energy values obtained in the present work, it is necessary to take into account the isotope effect of tritium, which is mainly manifested in an increase in the activation energy of the elementary act of free-radical substitution by 2.5-3.5 kcal/mole ([13]). Taking an average of 3 kcal/mole, we obtain from (6) and (7):

$$(E^{\text{H}} - E_p/2)_{\text{cyc}} = 9400 \text{ cal/mole},$$

$$(E^{\text{H}} - E_p/2)_{\text{hep}} = 10\,700 \text{ cal/mole}.$$

For gas-phase reactions of free radicals with hydrogen atoms of hydrocarbons, the magnitude of a similar difference usually lies within the range 9200-10 600 cal/mole, provided that the free electron of the radical and the hydrogen atom being abstracted are located at structurally equivalent carbon atoms (primary, secondary, etc.) ([4–7,9,12]). Comparing these values with those obtained in the present work, we conclude that in our case the liquid phase also exerts no specific influence on the activation energies of the elementary reactions. This conclusion is valid only for free-radical reactions proceeding in a medium of saturated hydrocarbons, as indicated by the data of studies ([14–16]).

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References

1. V. L. Antonovskii, I. V. Berezin, ZhFKh, **34**, 1286 (1960).
2. M. Levy, M. Szwarc, J. Am. Chem. Soc., **76**, 5981 (1954).
3. H. Simon, H. Daniel, J. E. Klebe, Angew. Chem., **71**, 303 (1959).
4. A. F. Trotmann-Dickenson, Quart. Rev., **7**, 198 (1953).

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5. P. B. Ayscough, J. Chem. Phys., **24**, 944 (1956).

6. P. J. Boddy, E. W. R. Steacie, Canad. J. Chem., **38**, 1576 (1960).

7. S. J. W. Price, K. O. Kutschke, Canad. J. Chem., **38**, 2128 (1960).

8. R. H. Riem, K. O. Kutschke, Canad. J. Chem., **38**, 2332 (1960).

9. J. A. Kerr, A. F. Trotmann-Dickenson, Trans. Farad. Soc., **55**, 921 (1959).

10. C. A. Heller, A. S. Gordon, J. Phys. Chem., **62**, 709 (1958).

11. G. H. Miller, E. W. R. Steacie, J. Am. Chem. Soc., **80**, 6486 (1958).

12. G. Giacometti, E. W. R. Steacie, Canad. J. Chem., **36**, 1493 (1958).

13. V. L. Antonovskii, I. V. Berezin, DAN, **134**, 860 (1960).

14. D. B. Peterson, G. J. Mains, J. Am. Chem. Soc., **81**, 3510 (1959).

15. D. H. Volman, L. W. Swanson, J. Am. Chem. Soc., **82**, 4141 (1960).

16. V. L. Antonovskii, I. V. Berezin, L. V. Shevelkova, DAN, **134**, 621 (1960).

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