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The reactivity of *tert*-butoxyl radicals in reactions of hydrogen abstraction and β-elimination

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The transition states of competing reactions of abstraction of the H atom from hydrocarbon molecules by *tert*-butoxyl radical and its β-elimination were studied by the semiempirical quantum-chemical AM1 method. The calculated activation enthalpy and entropy of these reactions correlate with the experimental values. A correlation between the reactivity in homolytic hydrogen abstraction and the parameters of the chemical structure of the reactants was found.

Key words: *tert*-butoxyl radical, transition state, reactivity, semiempirical method AM1.

Peroxide compounds are widely used as initiators in radical reactions. Thermal decomposition produces alkoxyl radicals, which either undergo β-elimination (reaction (1)) or are consumed mainly in H atom abstraction (reaction (2)):

$$Me_3CO^{\cdot} \longrightarrow Me_2CO + Me^{\cdot}, \qquad (1)$$

$$Me_3CO^{\cdot} + RH \longrightarrow Me_3COH + R^{\cdot}. \qquad (2)$$

The experimental determination of the activation parameters of these reactions is a difficult problem.[1] Therefore, it is of interest to develop calculation schemes, which allow these parameters to be calculated from the characteristics of the electronic structure of reactants.

It is known[2] that alkoxyl radicals are virtually not solvated in organic solvents, and their relative reactivity in the gas phase and solutions is almost the same. Therefore, reactions with their participation are convenient objects for quantum-chemical studies.

In this work, we studied the reactivity of *tert*-butoxyl radical in reactions (1) and (2) with alkanes, cycloalkanes, and arenes, whose experimental rate constants and, in some cases, activation parameters are known: *n*-C_5H_{12},[3] *n*-C_6H_{14},[3] *n*-C_7H_{16},[3,4] *cyclo*-C_6H_{12},[4,5,6] *cyclo*-C_6H_{10},[4,5,6] $Me_2CHCHMe_2$,[3,4,6] C_6H_6,[4,5] PhMe,[4,7,8] PhEt,[4,5] PhC_3H_7,[3,5] 1,4-Me_2Ph,[4,7,8] 1,3-Me_2Ph,[7,8] 1,2-Me_2Ph,[8] 1-Me-4-MeOPh,[7] 1,3,5-Me_3Ph,[5,9] 1-Me-3-ClPh,[7,8] 1-Me-4-ClPh,[8] 2-$EtC_{10}H_7$,[5] Ph_2CH_2,[4] and $PhCH_2Cl$.[10]

Calculation Procedure

Quantum-chemical calculations were performed in the AM1 approximation[11] (MOPAC 93 program[12,13]). This approximation was chosen because for the reactants under study the calculation of the standard enthalpy of formation ($\Delta H°_{298}$) gives a satisfactory agreement with the experimental values[14] and can be described by the following equation:

$$\Delta H°_{298}(\text{exp}) = -7.98(\pm 2.73) + 0.90(\pm 0.02)\Delta H°_{298}(\text{calc}).$$

The correlation coefficient is 0.994, and the standard error is 8.90 kJ mol^{-1}.

For the $Me_3CO^{\cdot}$ radical, the calculated enthalpy of formation is −83.68 kJ mol^{-1}, which agrees well with the experimental thermochemical value of −90.37 kJ mol^{-1}.[15]

Results and Discussion

Calculation of thermodynamic parameters of reactions (1) and (2). As follows from the results in Table 1, the formation of products in both reactions (1) and (2) is thermodynamically favorable. In reaction (1) the Gibbs free energy (ΔG_{298}) is determined by the entropy factor, and that in reaction (2) is determined by the enthalpy factor. Therefore, the following correlation between the rate constant and thermal effect of the reaction is fulfilled in the case of reaction (2):

$$\log k = -4.24(\pm 0.63) - 0.05(\pm 0.00)\Delta H_{298},$$

where k is the rate constant of reaction (2) at 298 K; correlation coefficient 0.966, standard error 0.66.

Transition state of reaction (1). The geometry of the reactants and reaction products as systems with open shells was optimized and the transition state (TS) of the reaction was localized in the approximation of the unrestricted Hartree—Fock self-consistent field (UHF SCF) method. The UHF wave function of the saddle point was tested by two methods. First, to reveal its nature, we performed numerically harmonic vibrational analysis by the calculation of the mass-weighed Hessian and ob-

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Table 1. ΔH_{298}, ΔS_{298}, and ΔG_{298} for reactions (1) and (2)

RH	ΔH_{298}	ΔG_{298}	ΔS_{298}
	kJ mol^{-1}		/J (mol K)$^{-1}$
$Me_3CO^{\cdot}$*	2.9	−42.7	153.5
PhEt	−133.9	−126.3	−12.5
cyclo-C_6H_{10}	−138.5	−139.7	2.5
PhMe	−114.6	−97.1	−29.7
cyclo-C_6H_{12}	−96.2	−101.2	8.8
C_6H_6	−1.7	−6.7	8.8
$Me_2CHCHMe_2$	−116.7	−142.7	47.7
1,4-Me_2Ph	−116.3	−142.2	43.5
$PhCHMe_2$	−148.1	−138.1	−16.7
1,2-Me_2Ph	−117.1	−117.6	0.8
1,3-Me_2Ph	−115.1	−128.9	23.0
Ph_2CH_2	−146.4	−185.3	64.8
1-Me-4-MeOPh	−117.6	−130.1	21.3
1,3,5-Me_3Ph	−115.5	−134.1	31.4
1-Me-3-ClPh	−114.6	−115.5	1.2
1-Me-4-ClPh	−116.3	−120.1	6.3
2-$EtC_{10}H_7$	_138.1	−139.2	3.8
n-C_5H_{12}	_101.2	133.9	54.8
n-C_6H_{14}	−104.2	−150.6	78.6
n-C_7H_{16}	−104.2	−154.8	85.3
$PhCH_2Cl$	−130.9	−128.0	−5.0

* The data for reaction (1).

Table 2. Experimental and calculated activation parameters of reaction (2), and $\nu^{\#}$ (cm^{-1}) — imaginary frequencies of vibrations in TS

RH	E_{exp}	log*A*	$\Delta H^{\#}$	$\Delta S^{\#}$	$\nu^{\#}$
cyclo-C_6H_{12}	28.1	10.9	59.4	−131.8	−2100
PhMe	21.3	9.2	54.8	−161.1	−2107
PhEt	23.0	10.0	53.5	−145.6	−2126
$PhCHMe_2$	21.8	9.7	54.8	−158.2	−2162
cyclo-C_6H_{10}	22.6	10.7	51.9	−140.2	−2164
C_6H_6	46.0	11.5	81.6	−123.4	−2309
$Me_2CHCHMe_2$	28.2	10.7	—	—	—
1,4-Me_2Ph	22.0	9.6	—	—	—

Note. E_{exp}/kJ mol^{-1} is experimental activation energies; log*A* is experimental logarithm of the pre-exponential factor; $\Delta H^{\#}$/kJ mol^{-1} is calculated activation energies; $\Delta S^{\#}$/J (mol K)$^{-1}$ is activation entropies.

tained frequencies and shapes of normal vibrations, one of which is imaginary and corresponds to the C—C vibration. Then we used the IRC method in the MOPAC 93 program to plot the internal coordinate of the reaction (UHF level) in the mass-weighed Cartesian coordinates (Fig. 1). The initial perturbation (equal to a quantum of the vibrational energy) along the normal coordinate and the reverse perturbation against the normal coordinate were used. Thus, the internal coordinate of the reaction was plotted beginning from the UHF-transition state along the reaction channels toward both the reactants and reaction products. A decrease in the potential energy in the path from TS is monotonic in both directions.

The reaction coordinate is a mode of the C—C vibration with the imaginary frequency $\nu^{\#} = -860$ cm^{-1}. In the TS the length of the cleaved C—C bond is 1.91 Å, and the fragments at both sides from this bond gain the configuration of the reaction products. The activation enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) are 67.4 kJ mol^{-1} and 6.7 J (mol K)$^{-1}$, respectively. The experimental activation energy is 67.0 kJ mol^{-1},[2] which surprisingly coincides with the obtained result.

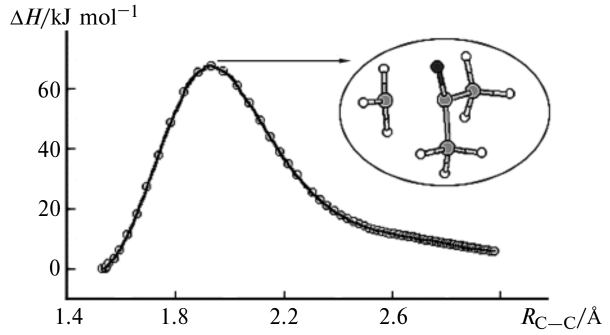

Fig. 1. Profile of reaction (1). The structure corresponding to the transition state of the reaction is presented in insert.

Transition state of reaction (2). The TS of reaction (2) was also calculated in the UHF SCF approximation. The initial geometry of TS was found by our method,[16] and then the saddle point was localized on the potential energy surface using the Bartel method incorporated in the MOPAC 93 program.

We calculated the TS of reaction (2) with the molecules containing different types of C—H bonds for which the experimental activation parameters are known. The obtained results are presented in Table 2.

The TS found have a structure close to that of the reactants (Fig. 2). The cleaved C—H bond lengthens by ~10%, whereas the elongation of the formed O—H bond is by 30—40% greater than that in the molecule of the final product. The reaction coordinate is a mode of the antisymmetrical vibration of atoms of the reaction center along the same line (C→H→←O). The corresponding frequencies of imaginary vibrations are presented in Table 2.

The found activation enthalpy is higher than the experimental value by ~30 kJ mol^{-1}. However, they demonstrate a good linear correlation

$$E_{exp} = -23.06(\pm 3.93) + 0.84(\pm 0.06)\,\Delta H^{\#}.$$

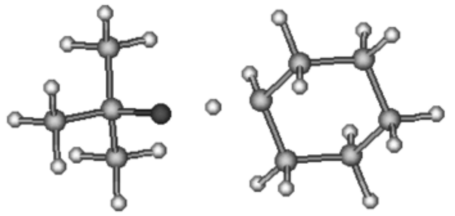

Fig. 2. Transition state of the reaction $Me_3CO^{\cdot}$ + *cyclo*-C_6H_{12} → Me_3COH + *cyclo*-$C_6H_{11}{}^{\cdot}$.

The correlation coefficient is 0.988, and the standard error is 1.63 kJ mol^{-1}. The same satisfactory correlation was found between logA and calculated values of activation entropy

$$\log A = 18.58(\pm 0.80) + 0.06(\pm 0.00)\ \Delta S^{\#}$$

with the correlation coefficient 0.981 and standard error 0.18.

Semiempirical relationships. We have previously found[16] that in the reaction similar to (2) involving the peroxyl radical instead of alkoxyl the reactivity of the molecules is determined by charge distribution on the atoms of the cleaved C—H bond and ionization potential of the molecule. A similar approach was used in this work.

The following correlation between the experimental activation energy and parameters that characterize the electron-donor properties of the molecules was obtained for the systems presented in Table 2

$$\begin{aligned} E_{\mathrm{exp}} = -42.55(\pm 4.99) &+279.97(\pm 39.65)Q_{\mathrm{H}} + \\ &+ 4.36(\pm 0.62)J, \end{aligned} \qquad (3)$$

where Q_H is the charge on the H atom of the reactive C—H bond, and J/eV is the ionization potential of the molecule. The correlation coefficient is 0.998, and the standard error is 0.78 kJ mol^{-1}.

The activation energies of reactions (2) (E_{calc}) were calculated by the obtained empirical correlation for all the systems. They are presented in Table 3.

In the TS of reaction (2) the number of vibrational degrees of freedom, which are deformation vibrations of the atoms of the reaction center (C...H...O), increases. It should be expected that these low-frequency vibrations characterize the activation entropy of reaction (2). Since the force constants are determined by charge distribution,[17] we can assume a correlation between the pre-exponential factor and charge distribution on the atoms of the reaction center.

Table 3. Activation parameters of reaction (2) calculated by Eqs. (3) and (4)

RH	E_{calc} /kJ mol^{-1}	logA_{calc}
PhEt	21.97	9.55
cyclo-C_6H_{10}	22.80	10.52
PhMe	21.09	9.13
cyclo-C_6H_{12}	28.18	11.07
C_6H_6	45.95	11.62
$Me_2C=CMe_2$	30.26	10.83
1,4-Me_2Ph	19.54	9.40
$PhCHMe_2$	22.93	9.81
n-C_6H_{14}	28.15	10.60
n-C_7H_{16}	27.96	10.69
1,2-Me_2Ph	20.21	9.40
1,3-Me_2Ph	20.29	9.39
1,3,5-Me_3Ph	20.14	9.65
Ph_2CH_2	24.09	9.93
1-Me-4-MeOPh	17.84	9.15
1-Me-3-ClPh	22.46	9.16
1-Me-4-ClPh	21.61	9.15
2-Et$C_{10}H_7$	18.36	9.55
n-C_5H_{12}	28.93	10.33
$PhCH_2Cl$	29.55	10.28

The pre-exponential factors were estimated from the activation energies calculated by Eq. (3) and experimental rate constants. The relationship between the pre-exponential factors and the parameters of the reaction center was determined in the following form:

$$\begin{aligned} \log A = 9.73(\pm 0.52) &+ 1.04(\pm 0.63)\log N_{\mathrm{C-H}} - \\ &- 0.46(\pm 0.06)P_i + 88.03(\pm 30.43)Q^2_{\mathrm{H}} - \\ &- 29.88(\pm 17.55)Q^2_{\mathrm{C}}, \end{aligned} \qquad (4)$$

where Q_H and Q_C are the charges on the H and C atoms of the reaction center, respectively; *Pi* is the parameter that characterizes the presence of the benzene ring in the α-position to the C—H bond (in fact, this parameter determines a type of the force field), which is accepted as equal to unity in the presence of the ring and to zero in the absence of the ring; and N_{C-H} is the number of equivalent C—H bonds (*i.e.*, the number of equiprobable reaction channels). The coefficient of multiple correlation is 0.975, and the standard error is 0.25. Then logA for all considered reactions were estimated by the obtained relationship (see Table 3).

Comparison of the experimental and calculated (by the Arrhenius equation taking into account Eqs. (3) and (4)) rate constants for the compounds presented in Table 1, for which experimental activation parameters are absent but the rate constants are known, showed a sufficiently good correlation between the experimental and calculated logk values for the reactions of hydrocarbon molecules with *tert*-butoxyl radical (123 constants measured within the 273—408 K temperature interval) (Fig. 3)

$$\log k(\mathrm{exp}) = 0.54(\pm 0.22) + 0.92(\pm 0.03)\log k(\mathrm{calc}).$$

The correlation coefficient is 0.920, and the standard error is ±0.26.

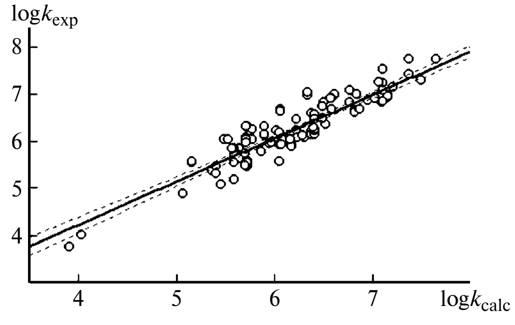

Fig. 3. Correlation between the experimental (logk_{exp}) and calculated (logk_{calc}) values of logarithms of the rate constants of reaction (2).

Thus, the obtained semiempirical equations describe completely the plots of the activation parameters *vs.* electron characteristics of the reactants and thermodynamic parameters of the reactions of *tert*-butoxyl radical monomolecular elimination and bimolecular abstraction. It is shown that *tert*-butoxyl radical at 298 K is thermodynamically unstable in reactions (1) and (2). The entropy factor is determining in reaction (1), and the enthalpy factor is determining in reaction (2). Therefore, it should be expected that the role of reaction (1) in chemical transformations of *tert*-butoxyl radical increases and that of reaction (2) decreases with temperature.

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