

The reactivity of ketyl and alkyl radicals in reactions with carbonyl compounds

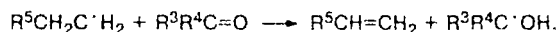
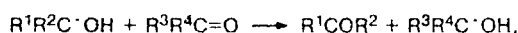
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A parabolic model of bimolecular radical reactions was used for analysis of the hydrogen transfer reactions of ketyl radicals: $>\text{C}\cdot\text{OH} + \text{R}^1\text{COR}^2 \rightarrow >\text{C}=\text{O} + \text{R}^1\text{R}^2\text{C}\cdot\text{OH}$. The parameters describing the reactivity of the reagents were calculated from the experimental data. The parameters that characterize the reactions of ketyl and alkyl radicals as hydrogen donors with olefins and with carbonyl compounds were obtained: $>\text{C}\cdot\text{OH} + \text{R}^1\text{CH}=\text{CH}_2 \rightarrow >\text{C}=\text{O} + \text{R}^1\text{C}\cdot\text{HCH}_3$; $>\text{R}^1\text{CH}=\text{CH}_2 + \text{R}^2\text{C}\cdot\text{HCH}_2\text{R}^3 \rightarrow \text{R}^2\text{C}\cdot\text{HCH}_3 + \text{R}^2\text{CH}=\text{CHR}^3$. These parameters were used to calculate the activation energies of these transformations. The kinetic parameters of reactions of hydrogen abstraction by free radicals and molecules (aldehydes, ketones, and quinones) from the C—H and O—H bonds were compared.

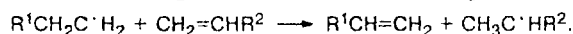
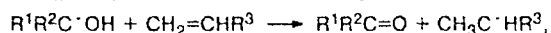
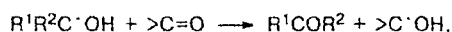
Key words: alkyl radical, ketyl radical, reactions with carbonyl compounds, hydrogen transfer, reactivity, parabolic model, activation energy, enthalpy of reaction.

Reactions of radical abstraction of a hydrogen atom by a free radical from a molecule are widely abundant and well studied. The majority of these reactions occur rapidly with heat release ($\Delta H < 0$) and low activation energies. Reverse reactions, in which the radical acts as the donor of the hydrogen atom and the molecule is its acceptor, are less known and poorly studied. They are, in particular, the reactions of ketyl and alkyl radicals with carbonyl compounds:



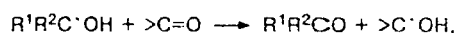
These transformations occur during photolysis and radiolysis of alcohols and carbonyl compounds¹ and are also intermediate stages in chain reactions of thermolysis, oxidation, and polymerization in the presence of alcohols, carbonyl compounds, and quinones.

A parabolic model is an efficient method for analysis of the reactivity of radicals and molecules in bimolecular reactions.² It makes it possible to classify the reactions of radical abstraction, divide them into groups, and to calculate and compare parameters characterizing the reactivity of each group. This method was used in this work to characterize and analyze the following processes:



Calculation procedure

For example, the parabolic model considers² the abstraction reaction



as the result of intersection of two potential curves, one of which describes the potential energy as a parabolic function of the amplitude of vibration of the cleaved (*i*th) bond and another curve describes that of the formed (*f*th) bond. The radical reaction is characterized by the following parameters:³

(1) enthalpy of the reaction ΔH_e that includes the difference of zero energies of reacting bonds

$$\Delta H_e = D_i - D_f + 0.5hL(v_i - v_f), \quad (1)$$

where D_i and D_f are the dissociation energies, and v_i and v_f are the frequencies of stretching vibrations of the *i*th and *f*th bonds, respectively; h is Planck's constant; and L is Avogadro's number;

(2) activation energy E_e that includes the energy of the zero vibration of the attacked bond and is related to the energy E determined experimentally by the simple correlation ($v_i = v$):

$$E_e = E + 0.5hLv - 0.5RT; \quad (2)$$

(3) distance r_e at which the attacked H atom is removed in the elementary reaction;

(4) parameters b_i and b_f which are dynamic characteristics of the cleaved ($b_i = \pi v_i(2\mu_i)^{1/2}$) and formed bonds ($b_f = \pi v_f(2\mu_f)^{1/2}$), where μ_i and μ_f are the reduced masses of atoms that form these bonds, and $2b^2$ is the force constant of the bond.

The five parameters listed above are related to each other by the following correlation:³

$$br_e = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2}, \quad (3)$$

where $\alpha = b_i/b_f$, $b = b_i$.

The br_e parameter makes it possible to calculate the characteristics of the whole group of reactions with $br_e = \text{const}$: the activation energy of the thermoneutral reaction E_{e0} ($\Delta H_e = 0$)

$$E_{e0} = (br_e)^2(1 + \alpha)^{-2} \quad (4)$$

As a rule, all reactions of the same group are characterized by the constant pre-exponential factor A , which allows one to calculate the E value through the rate constant (k) by the Arrhenius equation:

$$E = RT \ln(A/k) \quad (5)$$

The br_e parameter calculated from the experimental data can be used for calculation of the activation energy of any individual reaction belonging to this group.³ At $\alpha = 1$, when the bonds with the same force constants are cleaved and formed, the E_e value can be calculated from the equation

$$E_e^{1/2} = 0.5br_e + (2br_e)^{-1}\Delta H_e, \quad (6)$$

and at $\alpha \neq 1$ (different force constants of the cleaved and formed bonds), it can be calculated from the formula

$$E_e^{1/2} = br_e(1 - \alpha^2)^{-1}\{1 - \alpha[1 - (1 - \alpha^2)(br_e)^{-2}\Delta H_e]^{1/2}\} \quad (7)$$

Equations (6) and (7) are valid for reactions with enthalpy ΔH_e , which varies in the interval⁴ $\Delta H_{e,\min} < \Delta H_e < \Delta H_{e,\max}$. For highly exothermic reactions with $\Delta H_e < \Delta H_{e,\min}$, the activation energy is virtually equal to zero ($E = 0.5RT$), whereas for exothermic reactions with $\Delta H_e > \Delta H_{e,\max}$, $E = \Delta H + 0.5RT$. The limiting values of ΔH_e depend on the br_e parameter and energies of the zero vibration of the cleaved ($0.5h\nu_i$) and formed ($0.5h\nu_f$) bonds:⁴

$$\Delta H_{e,\min} = -(br_e/\alpha)^2 + 2br_e\alpha^{-2}(0.5h\nu_i)^{1/2} - 0.5(1 - \alpha^2)h\nu_i \quad (8)$$

$$\Delta H_{e,\max} = (br_e)^2 - 2br_e\alpha(0.5h\nu_f)^{1/2} + 0.5(\alpha^2 - 1)h\nu_f \quad (9)$$

For reactions with $\Delta H_e < \Delta H_{e,\min}$ and $\Delta H_e > \Delta H_{e,\max}$, the pre-exponential factor A depends on the ΔH_e value, since the higher $|\Delta H_e|$, the larger the collision cross section of particles:⁴

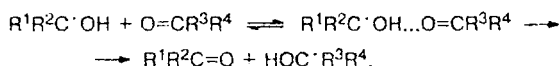
$$A = A_0\{1 + \beta[|\Delta H_e|^{1/2} - |\Delta H_{e,\min/\max}|^{1/2}]\}^2, \quad (10)$$

where $\beta = 1$ and 1.6 for the C...H...C and O...H...O transition states, respectively.

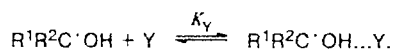
Results and Discussion

Reactions of ketyl radicals with carbonyl compounds

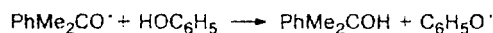
Since in the reaction of the ketyl radical with a carbonyl compound the hydrogen atom is transferred from one oxygen atom to another and hydroxyl-containing compounds form hydrogen bonds with these compounds, these reactions are preceded by the formation of the complex:⁵



In this mechanism, the reactions indicated should be characterized by a high pre-exponential factor A . In the present work, in the calculation of the activation energy by Eq. (5), we used $A = 2.5 \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ for the reaction in the liquid phase in the nonpolar solvent. In the polar solvent Y (alcohols, ketones, acetonitrile, etc.), ketyl radicals form a complex with the hydrogen bond:⁵



This decreases the concentration of free ketyl radicals involved in the hydrogen transfer reaction. The experimental values of rate constants of the reactions of hydrogen transfer from the ketyl radical to ketone or aldehyde at 298 K are presented in Table 1. These data were used for calculation of the activation energy E from Eq. (5). The concentration (fraction) of free ketyl groups in such solvents as alcohol, acetonitrile, and benzene was estimated as follows. The rate constants of the reaction



in different solvents at 298 K have been estimated previously¹⁰ by the pulse photolysis technique. The values obtained¹⁰ were used in this work as the ratio of the rate constants of the reaction in the given solvent and in CCl_4 (k/k_{CCl_4}) for estimation of the ratio $[R^1R^2C\cdot OH]/[R^1R^2C\cdot OH \cdots Y] = (1 + K_Y[Y])^{-1}$.

Y	CCl_4	C_6H_6	MeCN	Me_3COH
k/k_{CCl_4}	1	0.32	$6.7 \cdot 10^{-3}$	$4.2 \cdot 10^{-3}$

The results of calculation (values of the activation energy) are presented in Table 1. The br_e parameter characterizing the whole group of these reactions of H atom abstraction from the ketyl radical by the carbonyl compound was calculated by Eq. (3) using the following values: $\alpha = 1$ (the same force constant corresponds to the cleaved and formed O—H bonds), $0.5h\nu = 21.7 \text{ kJ mol}^{-1}$, $\Delta H_e = \Delta H$, since $\nu_i = \nu_f$ (see Eq. (1)). The br_e parameter has close values $br_e(\text{aver.}) = 12.88 \pm 0.31 \text{ (kJ mol}^{-1}\text{)}^{1/2}$, so that this group of reactions is characterized by the following parameters (see Eqs. (4), (8), and (9)):

α	br_e /(kJ mol ⁻¹) ^{1/2}	$r_e \cdot 10^{11}$ /m	E_{e0} kJ mol ⁻¹	$ \Delta H_{e,\min/\max} $ kJ mol ⁻¹
1	12.88	2.350	41.5	45.9

The br_e parameter can be used for calculation of activation energies of various reactions of this group. For this calculation, it is necessary to estimate the enthalpies of the corresponding reactions. The enthalpy of the reaction of the ketyl radical with carbonyl compound is equal to the difference of dissociation energies of the cleaved O—H bond of the ketyl radical $R^1R^2C\cdot OH$ and the formed O—H bond in the $R^3R^4C\cdot OH$ radical.

Table 1. Kinetic parameters of reactions of ketyl radicals with carbonyl compounds

Reaction	Medium	ΔH /kJ mol ⁻¹	k (298 K) /L mol ⁻¹ s ⁻¹	E /kJ mol ⁻¹	br_e /(kJ mol ⁻¹) ^{1/2}	Refer- ence
Me ₂ C [•] OH + Me(CH ₂) ₇ CHO	Me ₂ CHOH	0.0	$3.0 \cdot 10^3$	20.2	12.76	6
Me ₂ C [•] OH + PhCHO	Me ₂ CHOH	-28.6	$1.8 \cdot 10^5$	10.0	13.21	6
PhMeC [•] OH + PhCOPr	MeCN	0.0	$3.7 \cdot 10^3$	20.8	12.85	7
PhC [•] HOH + PhCHO	C ₆ H ₆	0.0	$8.0 \cdot 10^4$	22.9	13.18	8
4-Me ₃ CC ₆ H ₄ C [•] (OH)Ph + Ph ₂ CO	MeCN	0.0	$1.3 \cdot 10^4$	17.7	12.36	9

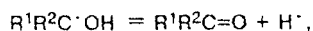
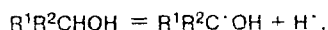
Note: k are experimental values; ΔH , E , and br_e were calculated by Eqs. (1)–(3).

Table 2. Enthalpies (ΔH) and activation energies (E) of reactions of hydrogen transfer from ketyl radicals to carbonyl compounds

R ¹ R ² C [•] OH	ΔH (E)/kJ mol ⁻¹						
	CH ₂ O	MeCHO	Me ₂ CO	PhCHO	PhMeCO	Ph ₂ CO	<i>p</i> -OC ₆ H ₄ O
H ₂ C [•] OH	0 (21.0)	14.4 (28.5)	18.1 (30.5)	-11.5 (15.4)	-7.8 (17.2)	-33.7 (5.8)	-110.6 (1.2)
MeC [•] HOH	-14.4 (14.1)	0 (21.0)	3.2 (22.8)	-25.9 (9.0)	-22.2 (10.6)	-48.1 (1.6)	-125.0 (1.2)
Me ₂ C [•] OH	-18.1 (12.4)	-3.7 (19.1)	0 (21.0)	-29.6 (7.5)	-25.9 (9.0)	-51.8 (1.2)	-128.7 (1.2)
PhC [•] HOH	11.5 (26.9)	25.9 (34.9)	28.6 (37.1)	0 (21.0)	3.7 (22.8)	-22.2 (1.6)	-99.1 (1.2)
PhMeC [•] OH	7.8 (25.0)	22.2 (32.8)	25.9 (34.9)	-3.7 (19.1)	0 (21.0)	-25.9 (9.0)	-102.8 (1.2)
Ph ₂ C [•] OH	33.7 (39.5)	48.1 (48.5)	51.8 (59.2)	22.2 (32.8)	25.9 (34.9)	0 (21.0)	-76.1 (1.2)
HOC ₆ H ₄ O [•]	110.6 (94.6)	125.0 (106.9)	128.7 (129.9)	99.1 (100.3)	102.8 (104.0)	76.9 (78.1)	0 (21.0)

Note. The E values were calculated by Eqs. (2) and (6).

The energy of dissociation of the O—H bond in ketyl radicals was calculated from the following thermochemical equations:



according to which $D(O-H) = -\Delta H(R^1R^2C^{\bullet}OH) + \Delta H(R^1R^2C=O) + \Delta H(H^{\bullet})$ and $\Delta H(R^1R^2C^{\bullet}OH) = \Delta H(R^1R^2CHOH) + D(C-H) - \Delta H(H^{\bullet})$. The enthalpies of formation of molecules in the gas phase¹¹ and dissociation energies of the corresponding C—H bonds in hydrocarbons¹² are taken from reference books, and $\Delta D = D(C-H)_{RH} - D(\alpha-C-H)_{ROH}$ have been determined previously.¹³ The $D(O-H)$ values thus calculated for the series of ketyl radicals are presented below.

Radical	$D(O-H)$ /kJ mol ⁻¹	Radical	$D(O-H)$ /kJ mol ⁻¹
H ₂ C [•] OH	117.5	Ph ₂ C [•] OH	151.2
MeC [•] HOH	103.1	PhC [•] HOH	129.0
Me ₂ C [•] OH	99.4	PhMeC [•] OH	125.3

For *p*-benzoquinone molecule,¹⁴ ([•]QH) $D(O-H) = 228.1$ kJ mol⁻¹. The activation energies E were calculated by Eqs. (2) and (6) at $\alpha = 1$. The results of calculation of ΔH and E are presented in Table 2. It is seen that the thermoneutral hydrogen transfer reaction occurs with a low activation energy (21 kJ mol⁻¹). Enthalpies of these reactions vary in a wide range: from -129 to 129 kJ mol⁻¹. The results of calculation of the reactions studied are close to the experimental values of activation energy (Table 3).

Table 3. Comparison of calculated by Eq. (6) and experimental activation energies of reactions of ketyl radicals with carbonyl compounds

Reaction	E /kJ mol ⁻¹		$ \Delta H $ /kJ mol ⁻¹
	calcula- tion	experi- ment	
Me ₂ C [•] OH + RCHO	21.0	20.2	0.8
Me ₂ C [•] OH + PhCHO	9.0	10.0	1.0
PhMeC [•] OH + PhRC [•] OH	21.0	20.8	0.2
PhC [•] HOH + PhCHO	21.0	22.9	1.9
PhC [•] HOH + Ph ₂ CO	21.0	17.7	3.3

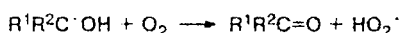
Table 4. Activation energies $E_{c0}/\text{kJ mol}^{-1}$ and parameters $br_e/(\text{kJ mol}^{-1})^{1/2}$ of reactions of radical abstraction with the O...H...O reaction center

Reaction	br_e	E_{c0}	Reference
$>\text{C}^{\cdot}\text{OH} + \text{O}=\text{C}<$	12.88	41.5	^a
$\text{ArO}^{\cdot} + \text{HOAr}$	12.61	39.7	15
$\text{R}^1\text{R}^2\text{NO}^{\cdot} + \text{HOAr}$	12.93	41.8	16
$\text{RO}_2^{\cdot} + \text{HOAr}$	13.46	45.3	15
$\text{R}^1\text{R}^2\text{NO}^{\cdot} + \text{HONR}^1\text{R}^2$	13.05	42.6	16
$\text{RO}_2^{\cdot} + \text{HONR}^1\text{R}^2$	13.50	45.6	16
$\text{RO}_2^{\cdot} + \text{HOOR}$	13.13	43.1	3
	$(13.08 \pm 0.29)^b$	$(42.8 \pm 1.9)^b$	

^a This work. ^b Average value.

We have analyzed previously the reactions of several oxygen-centered radicals with the hydroxyl groups of phenols¹⁵ ArOH, hydroxylamines¹⁶ R¹R²NOH, and hydroperoxides³ ROOH. The br_e and E_{c0} values of these reactions and those of the reactions of ketyl radicals with carbonyl compounds are compared in Table 4.

It is seen that all seven groups of reactions are characterized by very close values of the br_e and E_{c0} parameters. This regularity allows us to include the reaction of the ketyl radical with oxygen



into the series of the reaction considered for which $br_e = 12.88 (\text{kJ mol}^{-1})^{1/2}$. The dissociation energy of the H—O₂[·] bond is equal¹⁷ to 203.4 kJ mol⁻¹. The calculation showed that all ketyl radicals react with O₂ to yield a large amount of heat and, hence, $E = 0.5RT$. For strongly exothermic reactions, the pre-exponential factor A depends on $|\Delta H|$ (see above). The ΔH , $\log A$ (calculated by Eq. (10)), and k values (see Eq. (5)) are presented below for these reactions, and $A_0 = 5 \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ with account of the fact that an O₂ molecule attacks *via* any of its two oxygen atoms.

Radical	$-\Delta H$ /kJ mol ⁻¹	$\log A$	$k \cdot 10^{-10}$ /L mol ⁻¹ s ⁻¹
H ₂ C [·] OH	85.9	11.1	3.6
MeC [·] HOH	100.3	11.2	4.5
Me ₂ C [·] OH	104.0	11.3	5.7
PhC [·] HOH	74.4	10.9	2.3
Ph ₂ C [·] OH	52.2	10.2	0.45

It is seen that the rate constants of these reactions are close to the values characteristic of diffusion-controlled reactions in solution, so that the abstraction of the H atom can compete with the addition of oxygen to the ketyl radical. This implies that two types of peroxy radicals, namely HO₂[·] and R¹R²C(O₂[·])OH, are formed in parallel during the oxidation of the corresponding alcohol.

For the reaction of O₂ with H₂C[·]OH in the gas phase, the experimentally measured value¹⁸ is $k =$

$5.9 \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. Since the frequency of collisions of particles in the liquid phase is approximately fivefold higher than that in gas, the value of $3 \cdot 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ corresponds to this frequency in the liquid phase, which coincides with the result of the calculation ($3.6 \cdot 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$).

Obviously, the reaction center of the O...H...O type determines completely the activation barrier of the thermoneutral reaction of these seven groups of reactions. In turn, this indicates the identical geometry of the reaction center with very close O...H...O angles between the atoms (most likely, about 100°) for all compared groups of reactions, including those involving the ketyl radical. This conclusion does not agree with the sandwich (circular) structure of the transition state suggested previously⁶ for the reactions of the ketyl group with the carbonyl group.

Reactions of exchange of a hydrogen atom between ketyl radicals and olefins

Since ketyl radicals possess a pronounced reduction activity, it can be expected that they react rather rapidly with olefins to reduce them to alkyl radicals:



Experimental data for these reactions are lacking,^{19,20} however, their activation energies can be estimated using the equations and parameters of the parabolic model of bimolecular reactions.^{2,3} Let us compare the r_e and E_{c0} parameters for the reactions with the C...H...O radical center (where R[·] is the alkyl radical, $b = 4.70 \cdot 10^{11} (\text{kJ mol}^{-1})^{1/2} \text{ m}^{-1}$).

Reaction	$r_e \cdot 10^{11}/\text{m}$	$E_{c0}/\text{kJ mol}^{-1}$
R [·] + HOOR	3.80	62.5
R [·] + HOAr	3.80	62.5
R [·] + HONR ¹ R ²	3.66	58.0
HO [·] + RH	3.67	58.8

It is seen that all four groups of reactions have very close values of the r_e and E_{c0} parameters. The average value of the br_e parameter is $17.54 \pm 0.31 (\text{kJ mol}^{-1})^{1/2}$. It can be assumed that this series also contains reactions of ketyl radicals with olefins, where the same C...H...O reaction center is formed. Then using the increment $\Delta br_e = 17.54 - 13.08 = 4.46 (\text{kJ mol}^{-1})^{1/2}$, we obtain the parameter $br_e = 12.88 + 4.46 = 17.34 (\text{kJ mol}^{-1})^{1/2}$ for the description of the reactions of ketyl radicals with olefins. In the case where the ketyl radical reacts with olefin containing the phenyl group in the α -position and the reaction center of the transition state has the Ph—C=C...H...O structure, we use the parameter $br_e = 17.34 + 0.99 = 18.33 (\text{kJ mol}^{-1})^{1/2}$, where 0.99 is the increment caused by the influence of π -electrons of the aromatic rings on the transition state.³ In the reactions of ketyl radicals with benzene, there is a transition state with

the C=C=C...H...O reaction center, which is characterized by the increment³ $\Delta br_c = 1.30$ (kJ mol⁻¹)^{1/2}; for the calculation, we used the parameter $br_c = 17.34 + 1.30 = 18.64$ (kJ mol⁻¹)^{1/2}. For the reactions with the C...H...O reaction center,² $\alpha = 1.256$. The parameters characterizing the reactions of ketyl radicals with olefins (br_c /(kJ mol⁻¹)^{1/2}; E_{c0} /kJ mol⁻¹; $r_c \cdot 10^{11}$ /m; $-\Delta H_{c,min}$ /kJ mol⁻¹; $\Delta H_{c,max}$ /kJ mol⁻¹) are presented below.

Transition state	br_c	E_{c0}	$r_c \cdot 10^{11}$	$-\Delta H_{c,min}$	$\Delta H_{c,max}$
>C...O...H...C=C	17.34	59.1	3.689	75.7	129.0
>C-O...H...C=C=C=C	18.64	68.3	3.966	97.6	189.1
>C-O...H...C=CPh	18.33	66.0	3.900	92.3	153.9

The enthalpies of these reactions were calculated as the difference between the dissociation energies of the O—H bond of the ketyl radical and α -C—H bond in the alkyl radical formed from olefin. The $D(C-H)$ values were calculated in the same way as those for O—H bonds of ketyl radicals using the data in Refs. 11–13.

Radical	$D(C-H)$ /kJ mol ⁻¹	Radical	$D(C-H)$ /kJ mol ⁻¹
MeC·H ₂	151.5	CH ₂ =C·H	147.2
MeC·HMe	147.8	PhC·HMe	190.5
Me ₂ C·Me	152.1	Ph ₂ C·Me	237.0
MeC·HCH ₂ Me	138.0	cyclo-C ₆ H ₇ ·	108.8

The difference between the energies of zero vibrations for these reactions is equal to 5.1 kJ mol⁻¹ and $0.5h\nu = 21.7$ kJ mol⁻¹. The results of calculation of the enthalpies and activation energies of the reactions of ketyl radicals with olefins are presented in Table 5. The enthalpies of these reactions vary in a wide range: from -120 to +119 kJ mol⁻¹. This range is broader than the $\Delta H_{c,min} - \Delta H_{c,max}$ interval (see above), where Eq. (7) was used to calculate E (at $\Delta H_c < \Delta H_{c,min}$, $E = 0.5RT$, and at $\Delta H > \Delta H_{c,max}$, $E = \Delta H + 0.5RT$).

Reactions of hydrogen exchange between alkyl radicals and olefins

Alkyl radicals are well known to react readily at the double bond of olefin. This results in polymerization, oligomerization, or dimerization of olefins. At the same time, there are reactions in which alkyl radicals act as donors of hydrogen atoms, such as disproportionation reactions in which one alkyl radical serves as the acceptor and the second radical is the hydrogen donor. Similar reaction can occur between the alkyl radical and olefin, for example,



Here olefin acts as the acceptor, the alkyl radical acts as the donor of the hydrogen atom, and the C...H...C reaction center, which is similar to those in the reactions of alkyl radicals with C—H bonds of hydrocarbons, is formed in the transition state. The transition state in this center is affected (the activation energy increases) by the adjacent π -bonds.^{2,3} The following values of the br_c /(kJ mol⁻¹)^{1/2} parameter were obtained for the reactions $R^{\cdot} + R'H$ in the parabolic model: 17.23 for the aliphatic C...H...C reaction center, 18.11 for the alkylaromatic Ph—C...H...C center, and 18.86 for the allylic C=C—C...H...C center.^{2,3} These parameters and $\alpha = 1$ were used for calculation of the activation energy of reactions of the H atom transfer from the radical to olefin. The same approach as that for the reactions of ketyl radicals with olefins was used to calculate the enthalpy of the reaction. The results of calculation are presented in Table 6. The calculated data can be compared with the experimental values for the chain transfer reaction during polymerization of styrene. The H atom transfer from the macroradical to the monomer is most probable in this process.

Table 5. Enthalpies (ΔH) and activation energies (E) of reactions of hydrogen transfer from the ketyl radical to olefin

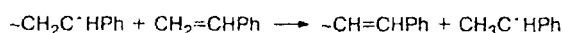
Olefin	ΔH (E)/kJ mol ⁻¹					
	C·H ₂ OH	MeC·HOH	Me ₂ C·H	PhC·HOH	PhMeC·OH	Ph ₂ C·OH
CH ₂ =CH ₂	-34.0 (22.9)	48.4 (16.1)	-52.1 (14.4)	-22.5 (35.7)	-26.2 (33.8)	-0.3 (47.8)
CH ₂ =CHMe	-50.3 (15.2)	-64.7 (9.0)	-68.4 (7.4)	-38.8 (27.5)	-42.5 (25.7)	-16.6 (38.8)
<i>trans</i> -MeCH=CHMe	-20.5 (29.8)	-34.9 (22.5)	-38.6 (20.7)	-9.0 (42.9)	-12.7 (40.9)	13.2 (55.5)
CH ₂ =CMe ₂	-34.6 (22.6)	-49.0 (15.8)	-52.7 (14.1)	-23.1 (35.4)	-26.8 (33.5)	-0.9 (47.4)
CH ₂ =CHPh	-73.0 (12.0)	-87.4 (6.2)	-91.1 (4.8)	-61.5 (16.9)	-65.2 (15.3)	-39.3 (71.5)
CH ₂ =CPh ₂	-119.5 (1.2)	-133.9 (1.2)	-137.6 (1.2)	-108.0 (1.2)	-111.7 (1.2)	-85.8 (6.8)
C ₆ H ₆	8.7 (55.2)	-5.7 (47.0)	-9.4 (45.0)	20.2 (62.0)	16.5 (59.8)	42.4 (75.7)

Note. The E values were calculated by Eqs. (2) and (7).

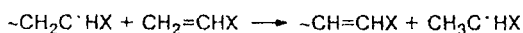
Table 6. Enthalpies (ΔH) and activation energies (E) of reactions of hydrogen transfer from the alkyl radical to olefin

Olefin	ΔH (E)/kJ mol ⁻¹					
	MeC [•] H ₂	MeEtC [•] H	Me ₂ CHC [•] H ₂	CH ₂ =C [•] H	PhMeC [•] H	C ₆ H ₇ [•]
CH ₂ =CH ₂	0 (58.0)	-13.5 (51.4)	-21.4 (47.7)	-4.3 (55.9)	39.0 (86.4)	-42.7 (52.7)
CH ₂ =CHMe	16.3 (66.4)	-29.8 (43.9)	-37.7 (40.4)	-20.6 (48.1)	22.7 (77.5)	-59.0 (45.7)
<i>trans</i> -MeCH=CHMe	13.5 (64.9)	0.0 (58.0)	-7.9 (54.1)	2.2 (62.7)	52.5 (94.1)	-29.2 (58.7)
CH ₂ =CMe ₂	-0.6 (57.7)	-14.1 (51.1)	-22.0 (47.6)	-4.9 (55.6)	38.4 (86.1)	-43.3 (52.4)
CH ₂ =CHPh	-39.0 (47.4)	-52.5 (41.6)	-60.4 (38.4)	-43.3 (45.6)	0.0 (65.8)	-81.7 (36.6)
CH ₂ =CPh ₂	-85.5 (28.6)	-99.0 (23.8)	-106.9 (21.0)	-89.8 (27.0)	-46.5 (44.2)	-128.2 (20.2)
C ₆ H ₆	42.7 (95.4)	29.2 (87.9)	21.3 (83.7)	38.4 (93.0)	81.7 (118.3)	0.0 (72.7)

Note. The E values were calculated by Eqs. (2) and (6).



According to the experimental data,²¹ the constant of chain transfer to the monomer during styrene polymerization is $C_M = k_M/k_p = 0.2\exp[-22.6/(RT)]$, and the rate constant of chain propagation is $k_p = 2.4 \cdot 10^8 \exp[-37.7/(RT)]$ L mol⁻¹ s⁻¹, from where the rate constant of chain transfer to the monomer is $k_M = k_p C_M = 4.8 \cdot 10^8 \exp[-60.3/(RT)]$ L mol⁻¹ s⁻¹. Similar mechanism of chain transfer to the monomer should be expected in the case of polymerization of vinyl chloride and acrylonitrile ($X = \text{Cl}, \text{CN}$).



For vinyl chloride,²¹ the constant of chain transfer to the monomer is $C_M = 125\exp[-30.5/(RT)]$, $k_p = 3.3 \cdot 10^6 \exp[-15.5/(RT)]$ L mol⁻¹ s⁻¹ and $k_M = k_p \cdot C_M = 4.1 \cdot 10^8 \exp[-46.0/(RT)]$ L mol⁻¹ s⁻¹. For acrylonitrile²¹ at 298 K, $C_M = 1 \cdot 10^{-5}$, $k_p = 382$ L mol⁻¹ s⁻¹ and $k_M = 3.8 \cdot 10^{-3}$ L mol⁻¹ s⁻¹. Since $k_M = A_M \exp[-E_M/(RT)]$, at $A_M = 4 \cdot 10^8$ L mol⁻¹ s⁻¹ we obtain $E_M = 62.9$ kJ mol⁻¹. Below we present the results of calculation of the activation energies of the chain transfer reactions considered (see Eqs. (2) and (6), $\alpha = 1$). The enthalpy of the reaction was calculated as the difference between the dissociation energies of the cleaved and formed bonds (for the description of this calculation and references, see above).

X	Cl	Ph	CN
$-\Delta H/\text{kJ mol}^{-1}$	15.5	8.6	10.0
$br_e/(\text{kJ mol}^{-1})^{1/2}$	17.23	18.11	18.11
$E_M(\text{calc})/\text{kJ mol}^{-1}$	50.5	61.5	60.9
$E_M(\text{exp})/\text{kJ mol}^{-1}$	46.0	60.3	62.9

It can be seen that the calculated and experimental values of activation energies of these reactions agree well (the average value is $|E_M(\text{calc}) - E_M(\text{exp})| =$

2.6 kJ mol⁻¹). Thus, the equations and parameters describing the activation energy of abstraction of the H atom from molecules also describe satisfactorily the inverse reaction of abstraction of the H atom by the molecule from the radical. This is evidence for similar structures of transition states in these processes, in particular, for a similar geometry of arrangement of atoms in the O...H...O, O...H...C, and C...H...C reaction centers for the reactions of abstraction of the H atom by both the radical from the molecule and the molecule from the radical. The quantum-chemical calculations of the activation energy of hydrogen transfer from the ethyl radical to ethylene give higher values ($E = 128$ kJ mol⁻¹ (see Ref. 22) and 112 kJ mol⁻¹ (see Ref. 23)). However, these E values are not obviously consistent with the experimental data on chain transfer in radical polymerization. The difference in the br_e and E_{e0} parameters for the reactions with the O...H...O, O...H...C, and C...H...C reaction centers has been considered previously² and can be explained by different triplet repulsions and different electronegativities of the O and C atoms in these reaction centers.

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