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Estimation of O–H Bond Dissociation Energies in Alcohols and Acids from Kinetic Data

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Abstract—The O–H bond dissociation energies ($D_{O–H}$) in five alcohols and six acids have been determined from experimental data (rate constants of radical reactions). The ratio of the rate constants of the reactions $R^1O^\bullet + RH \longrightarrow R^1OH + R^\bullet$ and $R^iO^\bullet + RH \longrightarrow R^iOH + R^\bullet$ and the intersecting parabolas method are used in the estimation procedure. The $D_{O–H}$ values are used to calculate the activation energies and rate constants for hydrogen abstraction from 2-methylbutane, butene-1, and cumene by alkoxyl and carboxyl radicals. The geometric parameters of the transition state are calculated for these reactions.

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The reactions of alkoxyl radicals $RO^\bullet$ play an important role in the liquid- and gas-phase oxidation of organic compounds [1, 2]. Alkoxyl radicals result from the decomposition of peroxides used as initiators [3] and of hydroperoxides (oxidation products) and from the disproportionation of tertiary peroxyl radicals [4, 5]. They are very reactive in radical abstraction reactions [5]:

$$R^iO^\bullet + RH \longrightarrow R^iOH + R^\bullet.$$

Carboxyl radicals $RC(O)O^\bullet$ result from the decomposition of diacyl peroxides used as initiators [4] and form in the reactions of peroxyl radicals with carboxylic acids [6]. Carboxyl radicals are also very reactive in radical abstraction reactions:

$$R^iCO_2^\bullet + RH \longrightarrow R^iCO_2H + R^\bullet.$$

The enthalpy ΔH of the reactions between $R^iO^\bullet$ and RH and between $R^iCO_2^\bullet$ and RH is equal to the difference between the dissociation energies of the breaking C–H and forming O–H bonds. The C–H bond strength is known for many hydrocarbons and organic compounds [3, 4, 7]. To the contrary, the strengths of the O–H bond in alcohols and carboxylic acids are known only for a few compounds [7].

The intersecting parabolas model (IPM) enables one to estimate $D_{O–H}$ provided that necessary experimental data are available [8, 9]. $D(R^iO–H)$ can be estimated from the difference between the dissociation energies of the $R^1O–H$ and $R^iO–H$ bonds (ΔD) if the former is known. In turn, ΔD can be calculated from the difference between the activation energies (ΔE) of the reactions $R^iO^\bullet$ + RH and $R^1O^\bullet$ + RH, where RH is the same hydrocarbon. ΔE can be derived from the ratio of the rate constants of these reactions. This method has been employed to estimate the dissociation energies of O–H bonds in alkyl hydroperoxides with different structures [10]. In this work, this method is applied to the totality of data available on the reactions of different alkoxyl and carboxyl radicals with hydrocarbons.

COMPUTATIONAL PROCEDURE

The same reaction center, namely, C…H…O, is involved in the abstraction reactions considered in this work. If the alkoxyl or carboxyl radicals are reacted with the same hydrocarbon RH, the reactions between $R^iO^\bullet$ and RH and between $R^1O^\bullet$ and RH are of the same class. Their activation energy and rate constant depend on the enthalpy of reaction and on the same set of parameters [9]. The difference between the activation energies of the reactions $R^iO^\bullet$ + RH (E_i, k_i) and $R^1O^\bullet$ + RH (E_1, k_1) is calculated using the formula [8]

$$E_i - E_1 = \Delta E = RT\ln(k_1/k_i). \qquad (1)$$

The difference between the dissociation energies (ΔD) of two O–H bonds in intersecting-parabolas terms is calculated by a formula taking into account the specific features of the class of reactions considered (parameters α and br_e) [8]:

$$\Delta D = D_i - D_1 = 2br_e\alpha^{-2}(\sqrt{E_{e,1}} - \sqrt{E_{e,1} + \Delta E}) - (\alpha^{-2} - 1)\Delta E, \qquad (2)$$

where α^2 is the ratio of the force constants of the C–H and O–H bonds, br_e is the parameter characterizing the given class of reactions, and $E_{e,1}$ is the activation energy of the reaction of $R^iO^\bullet$ with RH, including the zero-point energy of the breaking C–H bond. This activation energy is related to the rate constant k_1 as follows:

$$E_{e,1}, \text{kJ/mol} = RT\ln(nA/k_1) + 17.4 - 0.5RT, \quad (3)$$

where n is the number of equally reactive C–H bonds attacked in the RH molecule, A is the preexponential factor per attacked C–H bond (which has a fixed value throughout the class of reactions), 17.4 (kJ/mol) is the zero-point vibration energy of the C–H bond, and T (K) is the temperature at which k_1 was measured. The parameter α for all reactions between $R^iO^\bullet$ and RH is equal to 0.796 [3, 9].

The parameter br_e was calculated from experimental data, specifically, from the rate constants of the reactions of the 1,1-dimethylethoxyl radical with a number of hydrocarbons and the enthalpies of these reactions (Table 1) using the formula [9]

$$br_e = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2}. \quad (4)$$

The enthalpy of the reaction includes the difference between the zero-point energies of the breaking C–H and forming O–H bonds (–4.3 kJ/mol) and is calculated using the equation [9]

$$\Delta H_e, \text{kJ/mol} = D_{C-H} - D_{O-H} - 4.3. \quad (5)$$

The dissociation energy of the O–H bond in the alcohol Me_3COH was taken to be 434.9 kJ/mol [11]. The dissociation energies of the C–H bonds were taken from a handbook [3].

Calculated br_e data separately averaged for each class of reactions (R^1H = paraffins and cycloparaffins, R^2H = olefins, and R^3H = alkylarenes) are presented below:

Hydrocarbon	Paraffin	Olefin	Alkylarene
br_e, (kJ/mol)$^{1/2}$	12.73	13.96	13.54
A, l mol^{-1} s^{-1} ($RO^\bullet$)	1.0×10^9	1.0×10^8	1.0×10^8
A, l mol^{-1} s^{-1} ($RCO_2^\bullet$)	1.0×10^{10}	1.0×10^9	1.0×10^9

The preexponential factor was taken to be 1.0×10^9 l mol^{-1} s^{-1} for the reactions between and alkoxyl radical and the aliphatic C–H bond and 1.0×10^8 l mol^{-1} s^{-1} for the same reactions involving the C–H bond of an olefin or alkylarene [9]. The same values of br_e should be expected for the reactions between a carboxyl radical and the C–H bond. However, a carboxyl radical can attack the C–H bond by either O atom due to the delocalization of the free electron between the two oxygen atoms. For this reason, higher values of A were accepted for the carboxyl radicals (see above). The reaction of the benzoyloxyl radical with cyclohexane was used to validate these values. For this reaction, the rate constant of H abstraction is $k(297\text{ K}) = 3.0 \times 10^7$ l mol^{-1} s^{-1} [28], and the activation energies are E = 18.8 kJ/mol and E_e = 35.0 kJ/mol. The enthalpy of this reaction is $\Delta H_e = 408.8 - 439.3 - 4.3 = -34.8$ kJ/mol (formula (5)). Setting $A_{C-H} = 1.0 \times 10^{10}$ l mol^{-1} s^{-1}, we obtain, using formulas (3)–(5), br_e = 12.57 (kJ/mol)$^{1/2}$ for the reactions of this carboxyl radical with the C–H bond of the aliphatic hydrocarbon. Within the measurement error, this value coincides with br_e for the reactions of the 1,1-dimethylethoxyl radical (Table 1).

The O–H bond dissociation energies calculated for alcohols and acids with different structures were used to estimate activation energies and rate constants for the reactions of the corresponding alkoxyl and carboxyl radicals with 2-methylbutane (R^1H), butene-1 (R^2H), and cumene (R^3H). These calculations were carried out using the IPM formula [9]

$$E = 7.450(br_e)^2\left\{1 - 0.796\sqrt{1 - \frac{0.366\Delta H_e}{(br_e)^2}}\right\}^2 + 17.4 - 0.5RT, \quad (6)$$

in which the enthalpy of the reaction ΔH_e is calculated using formula (5); the values of D_{C-H} for the hydrocarbons are known [3]; and br_e characterizes the reactions of the alkoxyl radicals with R^1H, R^2H, or R^3H hydrocarbons (see above). Activation energy was calculated using Eq. (6), and rate constants were determined using the Arrhenius equation.

A semiempirical method for calculating transition state geometry for radical abstraction reactions in terms of the enthalpy and activation energy of reaction was developed in earlier studies [29, 30]. This method is a combination of the IPM and DFT methods. The essence of this method is that the bond elongation r_e derived from experimental data (ΔH and E) using formula (4) is correlated using quantum-chemical data. The interatomic distance C…H…O in the transition state of the reaction of $R^iO^\bullet$ with RH is the sum of three terms:

$$r(\text{C…H…O}) = r_{CH} + r_{OH} + \beta r_e, \quad (7)$$

where r_{CH} and r_{OH} are the bond lengths in the RH and R^iOH molecules, r_e is the elongation of these bonds in the transition state calculated by the IPM method using formula (4), and the correlation coefficient β makes the distance r(C…H…O) equal to the distance obtained by quantum-chemical calculations. The coefficient β was calculated in an earlier study [30]; for reactions involving the reaction center C…H…O, it takes a value of 1.44.

Since r_e can be expressed in terms of E_e, α, and b, the following formula is valid for the r(C…H…O) distance:

$$r(\text{C…H…O}) = r_{CH} + r_{OH} + \beta b^{-1}(\alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e}). \quad (8)$$

The position of the H atom in the reaction center of the transition state is characterized by distances $r^{\#}$(C…H) and $r^{\#}$(O…H). These distances depend on the activation energy E_e and enthalpy ΔH_e. They are expressed by the formulas [30]

Table 1. Rate constants and the parameters br_e calculated using formula (4) for the reactions of the 1,1-dimethylethoxyl radical with hydrocarbons of different classes

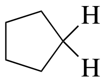
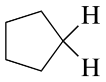
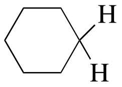
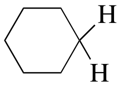
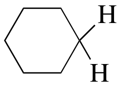
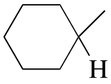
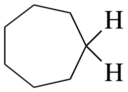
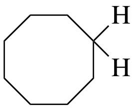
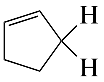
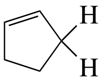
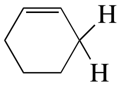
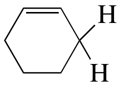
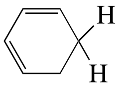
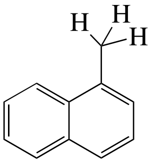
RH	n	T, K	k, l mol^{-1} s^{-1}	E_e, kJ/mol	$-\Delta H_e$, kJ/mol	br_e, (kJ/mol)$^{1/2}$	Reference
			$Me_3CO^{\bullet} + R^1H$, D_{O-H} = 434.9 kJ/mol [11]				
$Me(CH_2)_5Me$	10	408	1.20×10^7	38.5	27.2	12.66	[12]
$Me(CH_2)_5Me$	10	318	1.10×10^6	40.4	27.2	12.90	[13]
$Me_2CHCHMe_2$	2	320	1.25×10^6	35.7	39.2	12.86	[14]
	10	180	2.54×10^6	35.9	30.8	12.49	[15]
	10	333	3.18×10^6	38.3	30.8	12.81	[16]
	12	333	3.42×10^6	36.7	30.4	12.58	[16]
	12	357	6.56×10^6	36.2	30.4	12.51	[17]
	12	313	3.30×10^6	35.6	30.4	12.43	[18]
	1	408	3.50×10^6	34.9	43.7	12.96	[19]
	14	333	7.57×10^6	36.8	35.3	12.82	[16]
	16	333	7.57×10^6	37.2	37.3	12.97	[16]
					Mean br_e = 12.73 ± 0.19, (kJ/mol)$^{1/2}$		
			$MeCO^{\bullet} + R^2H$				
	4	313	9.10×10^6	26.0	96.7	13.92	[14]
	4	343	1.69×10^7	25.2	96.7	13.81	[17]
	4	300	5.80×10^6	26.8	97.7	14.06	[20]
	4	295	5.70×10^6	26.6	97.7	14.03	[21]
	4	295	4.20×10^7	21.7	108.0	13.72	[22]

Table 1. (Contd.)

RH	n	T, K	k, l mol^{-1} s^{-1}	E_e, kJ/mol	$-\Delta H_e$, kJ/mol	br_e, (kJ/mol)$^{1/2}$	Reference
$CH_2{=}CH(CH_2)_5Me$	2	300	1.50×10^6	28.4	89.4	13.97	[20]
$CH_2{=}CH(CH_2)_4C{=}CH_2$	4	295	2.30×10^6	28.8	89.4	14.02	[21]
E-MeCH=CHMe	6	313	2.18×10^6	30.7	82.4	14.01	[18]
$CH_2{=}C(CH_3)_2$	6	313	1.30×10^6	32.1	81.3	14.14	[18]
Mean br_e = 13.96 ± 0.12, (kJ/mol)$^{1/2}$							
$Me_3CO^{\bullet} + R^3H$							
$PhCH_3$	3	403	3.80×10^6	30.4	64.2	13.26	[23]
$PhCH_3$	3	400	3.47×10^6	30.6	64.2	13.28	[12]
$PhCH_3$	3	313	7.00×10^5	31.9	64.2	13.45	[24]
$PhCH_3$	3	343	1.40×10^6	31.3	64.2	13.37	[24]
$PhCH_3$	3	298	2.90×10^5	33.4	64.2	13.64	[14]
$PhCH_3$	3	318	4.20×10^5	33.5	64.2	13.66	[25]
$PhCH_3$	3	408	2.90×10^6	31.4	64.2	13.38	[26]
$PhCH_3$	3	295	2.30×10^5	33.8	64.2	13.69	[21]
$PhCH_3$	3	393	1.24×10^6	33.7	64.2	13.68	[27]
$PhCH_2CH_3$	2	273	3.60×10^5	30.6	75.1	13.71	[14]
$PhCH_2CH_3$	2	295	1.05×10^6	29.0	75.1	13.51	[21]
$PhMe_2CH$	1	318	1.20×10^6	27.8	84.5	13.71	[13]
$PhMe_2CH$	1	313	9.30×10^5	28.3	84.5	13.77	[28]
$PhMe_2CH$	1	408	7.90×10^6	24.3	84.5	13.23	[12]
	3	393	2.70×10^6	31.2	74.1	13.75	[27]
Mean br_e = 13.54 ± 0.19, (kJ/mol)$^{1/2}$							

$$r^{\#}(\mathrm{C}\ldots\mathrm{H}) = r_{\mathrm{CH}} + \beta b^{-1}\sqrt{E_e}, \tag{9}$$

$$r^{\#}(\mathrm{O}\ldots\mathrm{H}) = r_{\mathrm{OH}} + \alpha\beta b^{-1}\sqrt{E_e - \Delta H_e}. \tag{10}$$

These formulas were used in this study to calculate the geometric parameters of the reactions of different alkoxyl and carboxyl radicals with cumene (see below). The following bond lengths were used in the calculation: $r_{\mathrm{CH}} = 1.092 \times 10^{-10}$ m for the hydrocarbons, $r_{\mathrm{OH}} = 0.967 \times 10^{-10}$ m for the alcohols, and $r_{\mathrm{OH}} = 1.015 \times 10^{-10}$ for the acids [39] ($b = 37.43 \times 10^{10}$ kJ$^{1/2}$ mol$^{-1/2}$ m^{-1}).

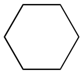
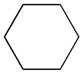
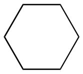
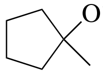
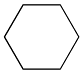
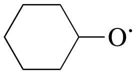
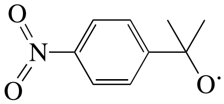
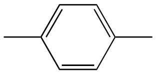
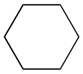
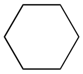
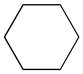
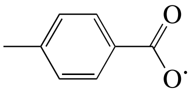
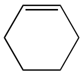
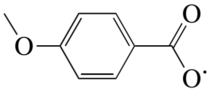
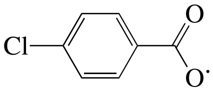
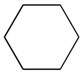
RESULTS AND DISCUSSION

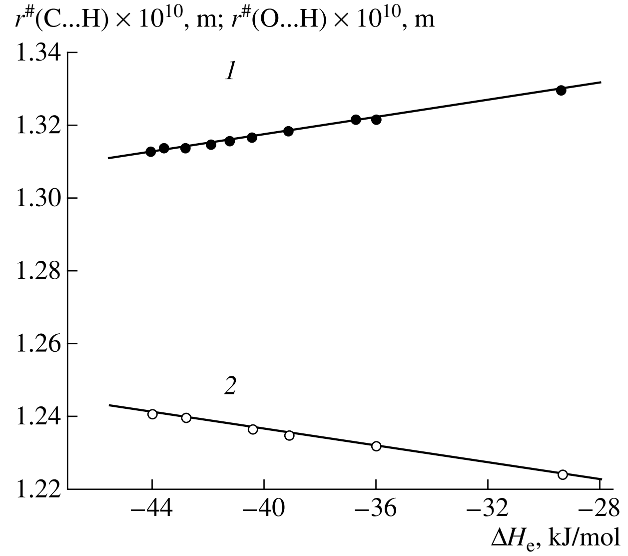
Dissociation Energies of the O–H Bonds in Alcohols and Acids

The dissociation energies of the O–H bonds in alcohols and acids calculated from kinetic data are presented in Table 2. The error of this estimation is ±2.5 kJ/mol [8].

The five alcohols listed in Table 2 are characterized by similar $D_{\mathrm{O-H}}$ values falling between 425 and 440 kJ/mol. Two estimates for cumyl alcohol were

Table 2. Rate constants of the reactions $R^iO^• + RH$ (k_i) and $R^1O^• + RH$ (k_1) and the O–H bond dissociation energies in alcohols ($D(R^iO–H)$) calculated using formulas (2) and (3)

$R^iO^•$	RH	T, K	k_1, $l\ mol^{-1}\ s^{-1}$	k_i, $l\ mol^{-1}\ s^{-1}$	ΔE, kJ/mol	E_{e1}, kJ/mol	ΔD, kJ/mol	$D_{O–H}$, kJ/mol	Reference
$R^1O^• = Me_3CO^•$ $D_{O–H}$ = 434.9 kJ/mol [11]									
$PhMe_2CO^•$		313	3.30×10^6	4.76×10^6	0.8	37.9	2.3	437.2	[31]
$PhMe_2CO^•$		313	3.30×10^6	6.51×10^6	1.5	37.9	4.3	439.2	[33]
Mean $D_{O–H}$ = 438.2 ± 1.0 kJ/mol									
$EtMe_2CO^•$		273	1.11×10^6	2.39×10^6	1.7	37.9	4.8	439.7	[31]
		273	1.11×10^6	2.56×10^5	–3.3	37.9	–9.8	425.1	[31]
	$PhCH_3$	298	2.90×10^5	4.60×10^5	1.1	33.5	3.6	438.5	[32]
		313	8.75×10^5	1.19×10^6	0.8	31.3	2.7	437.6	[34]
$R^1O^• = PhC(O)O^•$ $D_{O–H}$ = 439.3 kJ/mol [7]									
$PrOC(O)O^•$	$PhCH_3$	293	8.90×10^7	3.30×10^7	–2.4	26.5	–9.3	430.0	[35]
$PrOC(O)O^•$		293	2.80×10^7	1.58×10^7	–1.4	35.0	–4.3	435.0	[35]
Mean $D_{O–H}$ = 432.5 ± 2.5 kJ/mol									
$EtMeCHOCO_2^•$		293	2.80×10^7	1.05×10^7	–2.4	35.0	–7.4	431.9	[35]
Ph≡CC(O)O$^•$		293	2.80×10^7	2.00×10^7	–0.8	35.0	–2.4	436.9	[36]
		297	1.20×10^8	9.40×10^7	–0.6	30.5	–2.3	437.0	[37]
	$PhCH_3$	297	9.20×10^7	8.40×10^7	–0.2	26.5	–0.8	438.5	[38]
		297	3.00×10^7	1.20×10^7	–2.3	35.0	–7.1	432.2	[37]



Interatomic distances (*1*) $r^{\#}$(C…H) and (*2*) $r^{\#}$(O…H) in the transition state as a function of the enthalpy of reaction for the reactions between $R^iO^{\bullet}$ and R^1H (Table 3).

made using data of two works. They turned out to be very close: 439.2 and 437.2 kJ/mol. The O–H bond dissociation energy for 1,1-dimethylpropanol (439.7 kJ/mol) is close to the earlier determined value $D_{O–H}$ = 436 kJ/mol [11]. Our $D_{O–H}$ data are within the range of estimates obtained for other aliphatic alcohols. For instance, $D_{O–H}$ ranges between 431 and 440 kJ/mol for ethanol, from 435 to 443 kJ/mol for 2-propanol, and between 440 and 446 kJ/mol for 1,1-dimethylethanol [7].

For the six acids, the $D_{O–H}$ values fall in a rather narrow range of 432–438 kJ/mol. For propoxyformic acid, data of two works led to the close $D_{O–H}$ estimates of 430.0 and 435.0 kJ/mol. For the substituted benzoic acids, a slight change in the O–H bond dissociation energy is observed under the effect of the substituent and there is no symbasis between $D_{O–H}$ and the Hammett constant σ [39].

Substituent	Cl	H	CH_3	OCH_3
σ	0.062	0.0	–0.17	–0.268
$D_{O–H}$, kJ/mol	432.2	439.3	437.0	438.5

Calculation of the Kinetic and Geometric Parameters of the Reactions between O-Centered Radicals and Hydrocarbons

The O–H bond dissociation energies determined for several alcohols and acids were used to calculate the activation energies, rate constants, and geometric parameters of the transition state of the reactions of a number of oxygen-centered radicals with the following hydrocarbons: 2-methylbutane ($D_{C–H}$ = 400 kJ/mol), butene-1 ($D_{C–H}$ = 349.8 kJ/mol), and cumene ($D_{C–H}$ = 354.7 kJ/mol) [3]. The calculation procedure is described above. The data calculated for the reactions of the oxygen-centered radicals with 2-methylbutane are presented in Table 3.

All these reactions are exothermic. The activation energies of the reactions of the alkoxyl and carboxyl radicals with 2-methylbutane (reaction class $RO^{\bullet} + R^1H$) are 12 to 22 kJ/mol, and the enthalpies of these reactions are –36 to –44 kJ/mol. For all reactions of this class, the total elongation of the C–H and O–H bonds (that is, the change in the C…O distance, $\Delta r^{\#}$(C…H…O)) is 0.495 × 10^{-10} m. The interatomic distance r(C…H) lengthens and r(O…H) shortens with an increasing enthalpy of reaction (figure).

The plots of r(C…H) and r(O…H) versus ΔH_e are linear and are described by the equations

$$\Delta r^{\#}(\mathrm{C}\ldots\mathrm{H}) = F_{CH} + G_{CH}\Delta H_e, \qquad (11)$$

$$\Delta r^{\#}(\mathrm{O}\ldots\mathrm{H}) = F_{OH} - G_{OH}\Delta H_e. \qquad (12)$$

The coefficients F and G are given below.

Reaction	$F_{CH} \times 10^{10}$, m	$G_{CH} \times 10^{10}$, m mol J^{-1}	$F_{OH} \times 10^{10}$, m	$G_{OH} \times 10^{10}$, m mol J^{-1}
$RO^{\bullet} + Me_2CHEt$	0.272 ± 0.001	1.17 ± 0.02	0.223 ± 0.001	–1.17 ± 0.02
$RO^{\bullet} + CH_2{=}CHCH_2Me$	0.139 ± 0.001	0.96 ± 0.02	0.250 ± 0.001	–0.96 ± 0.02
$RO^{\bullet} + PhMe_2CH$	0.290 ± 0.001	1.08 ± 0.02	0.238 ± 0.001	–1.08 ± 0.02

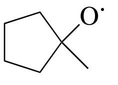
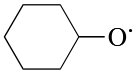
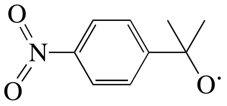
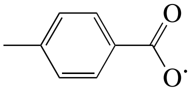
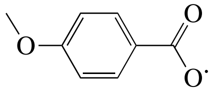
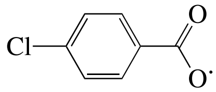
The data calculated for the reactions of the alkoxyl and carboxyl radicals with butene-1 are listed in Table 4.

The enthalpies of the reactions of the alkoxyl and carboxyl radicals with butene-1 (reaction class $RO^{\bullet} + R^2H$) range from –80 to –94 kJ/mol. The activation energies of these reactions are 11 to 15 kJ/mol. The total elongation of the C–H and O–H bonds is $\Delta r^{\#}$(C…H…O) = 0.544 × 10^{-10} m for all reactions of this class. The interatomic distance r(C…H) lengthens with an increase in the enthalpy of reaction, while r(O…H) shortens. The plots of r(C…H) and r(O…H) versus ΔH_e are also linear and are described by Eqs. (11) and (12).

The data calculated for the reactions of the alkoxyl and carboxyl radicals with cumene are presented in Table 5.

For the reactions of the oxygen-centered radicals with cumene (reaction class $RO^{\bullet} + R^3H$), the enthalpy

Table 3. Enthalpies, activation energies, rate constants, and interatomic distances in the transition state of the reactions of the alkoxyl and carboxyl radicals with 2-methylbutane calculated by the intersecting parabolas method

$R^iO^•$	$-\Delta H_e$, kJ/mol	E, kJ/mol	k(353 K), l mol^{-1} s^{-1}	$r^{\#}$(C...H) × 10^{10}, m	$r^{\#}$(O...H) × 10^{10}, m
			$R^iO^• + Me_2CHCH_2CH_3$		
$CH_3O^•$	36.0	19.9	1.13×10^6	1.322	1.232
$MeCH_2O^•$	36.7	19.7	1.23×10^6	1.322	1.232
$Me_2CHO^•$	36.2	19.8	1.16×10^6	1.322	1.232
$EtMeCHO^•$	39.1	18.8	1.65×10^6	1.319	1.235
$Me_3CO^•$	39.2	18.8	1.67×10^6	1.319	1.235
$EtMe_2CO^•$	44.0	17.1	2.94×10^6	1.313	1.241
$Me_3CCH_2O^•$	40.4	18.4	1.92×10^6	1.317	1.237
	29.4	22.3	4.95×10^5	1.330	1.224
	42.8	17.5	2.56×10^6	1.314	1.240
$PhMe_2CO^•$	42.5	17.6	2.47×10^6	1.314	1.240
	41.9	17.8	2.30×10^6	1.315	1.239
			$R^iC(O)O^• + Me_2CHCH_2CH_3$		
$PrOC(O)O^•$	36.8	19.6	2.49×10^6	1.321	1.281
$EtMeCHOC(O)O^•$	36.2	19.8	2.32×10^6	1.322	1.280
$PhC{\equiv}CC(O)O^•$	41.2	18.1	4.24×10^6	1.316	1.286
$PhC(O)O^•$	43.6	17.2	5.62×10^6	1.314	1.288
	41.3	18.0	4.29×10^6	1.316	1.286
	42.8	17.5	5.12×10^6	1.314	1.288
	36.5	19.7	2.40×10^6	1.322	1.280

varies between –81 and –89 kJ/mol. The activation energy is 9–13 kJ/mol. The total elongation of the C–H and O–H bonds in the transition state is $\Delta r^{\#}$(C...H...O) = 0.528×10^{-10} m for all reactions of this class. The interatomic distance r(C...H) lengthens with an increase in the reaction enthalpy, while r(O...H) shortens. The plots of r(C...H) and r(O...H) versus ΔH_e are linear and are described by Eqs. (11) and (12).

Thus, we have estimated the dissociation energies of the O–H bonds for a number of alcohols and acids. The values obtained agree with the D_{O-H} values for similar compounds with simpler structures. The activation energies, rate constants, and interatomic distances in the transition state have been calculated for the reactions of the alkoxyl and carboxyl radicals with three hydrocarbons from different classes.

Table 4. Enthalpies, activation energies, rate constants, and interatomic distances in the transition state of the reactions of the alkoxyl and carboxyl radicals with butene-1 calculated by the intersecting parabolas method

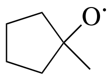
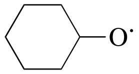
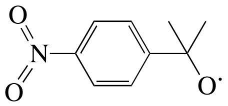
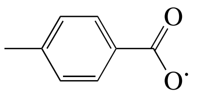
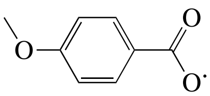
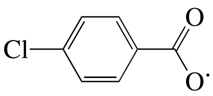
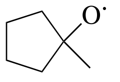
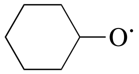
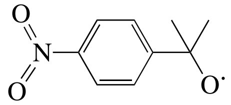
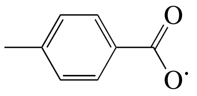
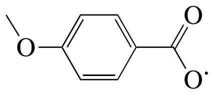
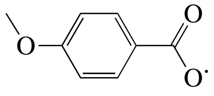
$R^iO^\bullet$	$-\Delta H_e$, kJ/mol	E, kJ/mol	k(353 K), $l\ mol^{-1}\ s^{-1}$	$r^{\#}$(C…H) × 10^{10}, m	$r^{\#}$(O…H) × 10^{10}, m
$R^iO^\bullet + CH_2{=}CHCH_2CH_3$					
$CH_3O^\bullet$	86.2	13.3	2.12×10^6	1.300	1.303
$MeCH_2O^\bullet$	86.9	13.1	2.27×10^6	1.209	1.304
$Me_2CHO^\bullet$	86.4	13.3	2.16×10^6	1.300	1.303
$EtMeCHO^\bullet$	89.3	12.5	2.86×10^6	1.297	1.316
$Me_3CCH_2O^\bullet$	90.6	12.1	3.24×10^6	1.296	1.307
$Me_3CO^\bullet$	89.4	12.4	2.89×10^6	1.297	1.306
$EtMe_2CO^\bullet$	94.2	11.1	4.55×10^6	1.292	1.311
	79.6	15.3	1.10×10^6	1.307	1.296
	93.0	11.4	4.07×10^6	1.293	1.310
$PhMe_2CO^\bullet$	92.7	11.5	3.95×10^6	1.293	1.310
	92.1	11.7	3.74×10^6	1.294	1.309
$R^iC(O)O^\bullet + CH_2{=}CHCH_2CH_3$					
$PrOC(O)O^\bullet$	87.0	13.1	4.59×10^6	1.299	1.352
$EtMeCHOC(O)O^\bullet$	86.4	14.8	2.60×10^6	1.230	1.351
$PhC{\equiv}CC(O)O^\bullet$	91.4	13.4	4.20×10^6	1.295	1.356
$PhC(O)O^\bullet$	93.8	12.7	5.26×10^6	1.292	1.359
	91.5	13.3	4.24×10^6	1.295	1.357
	93.0	12.9	4.88×10^6	1.293	1.358
	86.7	14.7	2.67×10^6	1.230	1.351

Table 5. Enthalpies, activation energies, rate constants, and interatomic distances in the transition state of the reactions of the alkoxyl and carboxyl radicals with cumene calculated by the intersecting parabolas method

$R^iO^\bullet$	$-\Delta H_e$, kJ/mol	E, kJ/mol	k(353 K), $l\ mol^{-1}\ s^{-1}$	$r^{\#}(C\ldots H) \times 10^{10}$, m	$r^{\#}(O\ldots H) \times 10^{10}$, m
$R^iO^\bullet + PhMe_2CH$					
$CH_3O^\bullet$	81.3	11.5	1.95×10^7	1.294	1.293
$MeCH_2O^\bullet$	82.0	11.3	2.09×10^7	1.293	1.294
$Me_2CHO^\bullet$	81.5	11.4	1.99×10^7	1.293	1.294
$EtMeCHO^\bullet$	84.4	10.7	2.64×10^7	1.290	1.297
$Me_3CCH_2O^\bullet$	85.7	10.3	2.96×10^7	1.289	1.298
$Me_3CO^\bullet$	84.5	10.6	2.66×10^7	1.290	1.297
$EtMe_2CO^\bullet$	89.3	9.3	4.18×10^7	1.285	1.302
	74.7	13.5	1.01×10^7	1.301	1.286
	88.1	9.6	3.74×10^7	1.287	1.300
$PhMe_2CO^\bullet$	87.8	9.7	3.63×10^7	1.287	1.300
	87.2	9.9	3.44×10^7	1.287	1.300
$R^iC(O)O^\bullet + PhMe_2CH$					
$PrOC(O)O^\bullet$	82.1	11.3	4.23×10^7	1.293	1.342
$EtMeCHOC(O)O^\bullet$	81.5	11.5	3.99×10^7	1.293	1.342
$PhC{\equiv}CC(O)O^\bullet$	86.5	10.1	5.43×10^7	1.288	1.347
$PhC(O)O^\bullet$	88.9	9.4	8.06×10^7	1.286	1.349
	86.6	10.1	6.50×10^7	1.288	1.347
	88.1	9.6	7.48×10^7	1.287	1.349
	81.8	11.4	4.10×10^7	1.293	1.342

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