Polar and solvation effects in reactions of oxygen atoms and hydroxyl and alkoxyl radicals with oxygen-containing compounds

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Experimental data on the activation energies of reactions of H-abstraction from oxygen-containing compounds by oxygen atoms and hydroxyl and alkoxyl radicals in the gas and liquid phases have been analyzed by means of the parabolic model of the transition state. The contribution of polar interaction to the activation energies of the reactions has been calculated. The contribution of solvation to the activation energy has been calculated by comparison of the reaction parameters of the respective reaction in the liquid and gas phases.

Key words: alkoxyl radical, oxygen atom, hydroxyl radical, rate constant, parabolic model, transition state, polar effect, radical abstraction, solvation, activation energy.

A great deal of research is devoted to the effect of polarity in chemical reactions, in particular, the influence of a polar medium on radical reactions has been considered in monographs.[1,2] Difficulties arise in the comparison of the reactivity of polar and nonpolar molecules toward free radicals. The insertion of a polar group into the hydrocarbon molecule changes the strength of the neighboring C—H bonds ($D_{\mathrm{R-H}}$) affecting, clearly, the heat of the reaction.

The parabolic model of radical abstraction [3,4]

$$\mathrm{X^{\cdot} + RH \rightarrow XH + R^{\cdot}}$$

treats the transition state as the result of the interception of two unperturbed potential curves (Fig. 1). One of the curves represents the dependence of the potential energy U_i on the amplitude of atomic vibration along the breaking bond (i), and the other, the dependence of U_i on the amplitude of atomic vibration along a forming bond (f). The oscillations of the atoms are, probably, harmonic in character, so, $U_i^{1/2} = b_i x_i$ and $U_i^{1/2} = b_f x_f$, and the atoms taking part in an elementary act are except the attacked H atom, at the fixed distance r_e (see Fig. 1). The transition states are assumed to be the result of the interception of the two undisturbed potential curves. Activation energy of the elementary act of H-abstraction may be expressed through the physical characteristics of the breaking and forming bonds, and, depending on the type of these bonds, all various reactions of radical abstraction can be divided into classes. Each class is characterized by two coefficients

$$b_i = \pi\nu_i(2\mu_i)^{1/2} \text{ and } b_f = \pi\nu_f(2\mu_f)^{1/2},$$

where ν_i and ν_f are the frequencies of the valence vibrations of the breaking and forming bonds, and μ_i and μ_f are the effective masses of the atoms forming these bonds. Each elementary reaction is further defined by enthalpy ΔH_e:

$$\Delta H_e = D_i - D_f + 0.5hL(\nu_i - \nu_f), \qquad (1)$$

where D_i and D_f are the energies of breaking and forming bonds, and h and L are Planck's constant and Avogadro's number, respectively, as well as by the activation energy E_e connected with the experimentally determining E value by means of the relation:

$$E_e = E + 0.5(h\nu_i L - RT). \qquad (2)$$

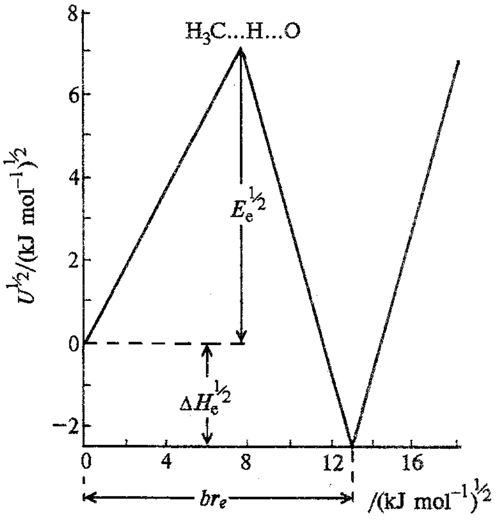

Fig. 1. Energetic profile of the O + CH$_4$ reaction (parabolic model).

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Table 1. Kinetic parameters of the reaction of oxygen atoms with oxygen-containing compounds in the gas phase[6]

RH	$-\Delta H_e$ /kJ mol^{-1}	k(298 K) /L mol^{-1} s^{-1}	Number of measurements (n)	E_e /kJ mol^{-1}	br_e /(kJ mol^{-1})$^{1/2}$	ΔE_μ
CH_4	6.0	$6.1 \cdot 10^3$	8	52.80	13.11	0.0
CH_3OH	36.6	$4.61 \cdot 10^6$	4	35.65	12.55	−4.6
CH_3CH_2OH	39.9	$3.24 \cdot 10^7$	3	29.80	11.92	−9.5
$(CH_3)_2CHOH$	50.2	$4.0 \cdot 10^7$	1	27.57	12.08	−8.2
$(CH_3)_3COH$	14.0	$3.16 \cdot 10^6$	2	39.30	11.92	−9.5
$(CH_3)_2O$	43.4	$2.94 \cdot 10^7$	3	32.77	12.48	−5.1
$(CH_3CH_2)_2O$	48.7	$7.3 \cdot 10^7$	1	29.51	12.28	−6.7
CH_2O	63.0	$9.67 \cdot 10^7$	6	27.10	12.55	−4.6
CH_3CHO	67.1	$2.65 \cdot 10^8$	3	22.85	12.12	−7.9
CH_3COCH_3	38.3	$4.47 \cdot 10^5$	5	43.15	13.55	−9.4
$CH_3COCH_2CH_3$	46.2	$6.34 \cdot 10^6$	2	33.85	12.74	−16.1
$(CH_3CH_2)_2CO$	46.2	$1.02 \cdot 10^7$	2	34.39	12.81	−15.6
c-$C_6H_{10}O$	49.8	$1.45 \cdot 10^7$	2	33.52	12.85	−15.2
$CH_3C(O)OCH_3$	38.3	$6.20 \cdot 10^5$	3	40.62	13.25	1.2
$CH_3C(O)OCH_2CH_3$	46.3	$3.23 \cdot 10^6$	2	35.52	12.96	−1.2

Each group of reactions of one class is characterized by the parameter $br_e = b_i r_e$ which is calculated using the parameter E_e and ΔH_e parameters for the separate reaction according to the following expression ($\alpha = b_i/b_f$):[4]

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

If the interaction of polar groups occurs in the transition state, this will affect the value of br_e. The contribution of the polar interaction to the activation energy can be estimated by comparing between the parameter $(br_e)_\mu$ for the reaction of a radical with a polar compound $R_\mu H$ and the parameter $(br_e)_{RH}$ of its nonpolar analog (for example, for MeOH and CH_4). This contribution was estimated according to the following expression:[5]

$$\Delta E_\mu = [(br_e)^2_\mu - (br_e)^2_{RH}]/(1 + \alpha)^2. \qquad (4)$$

It follows from Eq. (4) that the contribution of the polar interaction to the activation energy depends on the parameter r_e as well as on the coefficients b_i and b_f ($\alpha = b_i/b_f$).

Results and Discussion

The data on the gas phase reactions (rate constants and activation energies) were taken from the database.[6] In order to decrease the scatter in the data, the value of the activation energy was calculated using the rate constant k and the pre-exponential factor A according to the formula:

$$E = RT \cdot \ln(A/k).$$

In the case of O + RH, the pre-exponential factor A is 4×10^9 L mol^{-1} s^{-1} in the calculation for one reacting C—H bond. The energies of the C—H bond which are necessary for the calculation of ΔH_e are taken from Refs. 7, 8. In the case of this reaction, the coefficient $\alpha = b_i/b_f = 0.774$. The initial data and results of the calculation of br_e and ΔE_μ for reactions of atomic oxygen are given in Table 1. The ΔE_μ values were calculated according to Eq. (4). For alcohol, aldehydes and ethers the comparison with the reaction of the C—H bond of a paraffinic hydrocarbon was carried out: $(br_e)_{RH} = 13.11$ (kJ mol^{-1})$^{1/2}$. Ketones were compared with olefins: $(br_e)_{RH} = 14.30$ (kJ mol^{-1})$^{1/2}$. From the column of ΔE_μ values one can see that the polar interaction in all of the considered reactions decreases the activation barrier, and only for esters is this effect absent (the error in the calculation of ΔE_μ is 1.5 kJ mol^{-1}). Probably, this is connected with the competitive attack of oxygen atoms on the alcohol or acid residues, and different br_e parameters (in other reactions) are typical for these reaction sites. The data obtained make it possible to estimate the contributions of the polar effect ΔE_μ and the enthalpy changes tjat occur when functional groups are inserted into a molecule of a particular hydrocarbon. This contribution of enthalpy change to activation energy may be represented as the difference $\Delta E = E_{e\mu} - 49$ (kJ mol^{-1}), where $E_{e\mu}$ is the activation energy of the reaction of an O atom with given compounds, and ethane is the hydrocarbon used for comparison (for which $E_e = 49$ KJ mol^{-1} calculated according to Eq. (3), parameter $br_e = 13.11$ (kJ mol^{-1})$^{1/2}$ and $\Delta H_e = -14$ (kJ cal^{-1})$^{1/2}$. The results of the calculation of the energies (kJ mol^{-1}) and μ (Debye) are given below.

	CH_3CH_2OH	$(CH_3CH_2)_2O$	CH_3CHO	CH_3COCH_3
E_e	29.8	29.5	22.8	43.2
$E_e - 49$	−19.2	−19.5	−26.2	−5.8
ΔE_μ	−9.5(33 %)	−6.7(26 %)	−7.9(23 %)	−9.4(62 %)
μ	1.68	1.17	2.69	2.85
$100(\Delta r_e/r_e)$ (%)	−9.0	−6.0	−8.0	−5.0

Table 2. Kinetic parameters of the reaction of hydroxyl with oxygen-containing compounds in the gas phase[6] and in aqueous solution[9]

RH	$-\Delta H_e$ /kJ mol^{-1}	Medium	$k \cdot 10^{-8}$ (298 K) /L mol^{-1} s^{-1}	Number of measurements (*n*)	E_e /kJ mol^{-1}	br_e /(kJ $mol^{-1})^{1/2}$	ΔE_μ /kJ mol^{-1}
CH_4	64.4	Gas	0.047	15	36.30	13.95	0
CH_4	64.4	H_2O	1.1	2	32.44	13.49	0
CH_3CH_3	84.4	Gas	1.6	33	28.59	13.74	0
CH_3CH_3	84.4	H_2O	18.0	1	26.57	13.48	0
$CH_3CH_2CH_3$	100.3	Gas	5.8	6	22.67	13.52	0
$CH_3CH_2CH_3$	100.3	H_2O	36.0	1	22.13	13.44	0
$CH_3(CH_2)_2CH_3$	99.5	H_2O	46.0	1	23.24	13.57	0
$(CH_3)_3CH$	110.6	Gas	13.5	7	18.85	13.33	0
c-C_5H_{10}	107.4	Gas	31.1	8	22.49	13.75	0
$(CH_3)_4C$	84.4	Gas	5.4	9	27.29	13.57	0
$C_6H_5CH_3$	134.6	Gas	1.2	2	25.75	15.08	0
c-C_6H_{10}	154.6	H_2O	88.0	1	21.63	15.14	0
CH_3OH	107.0	Gas.	5.6	3	23.75	13.91	2.4
CH_3OH	107.0	H_2O	9.7	9	26.38	14.26	6.6
CH_3CH_2OH	110.3	Gas	17.0	10	20.00	13.48	−1.3
CH_3CH_2OH	110.3	H_2O	19.0	14	23.71	14.01	4.4
$(CH_3)_2CHOH$	120.6	Gas	35.3	4	16.47	13.31	−2.7
$(CH_3)_2CHOH$	120.6	H_2O	19.0	5	22.00	14.12	5.3
$(CH_3)_3COH$	84.4	Gas	7.0	1	25.92	13.39	−2.0
$(CH_3)_3COH$	84.4	H_2O	6.0	3	30.29	14.13	5.4
CH_2OHCH_2OH	117.5	H_2O	18.0	4	25.56	14.50	8.7
$CH_3(CHOH)_2CH_3$	120.6	H_2O	13.0	1	24.65	14.49	8.6
$CH_2OHCHOHCH_2OH$	120.6	H_2O	19.0	1	22.00	14.12	5.3
$CH_2OH(CH_2)_2CH_2OH$	110.3	H_2O	32.0	1	24.14	14.07	4.9
$CH_2OH(CH_2)_3CH_2OH$	110.3	H_2O	36.0	1	23.84	14.03	4.5
CH_3OCH_3	113.8	Gas	19.6	2	22.37	13.95	2.8
CH_3OCH_3	113.8	H_2O	10.0	4	28.02	14.70	10.6
$(CH_3CH_2)_2O$	119.1	Gas	80.8	2	17.85	13.47	−1.4
$(CH_3CH_2)_2O$	119.1	H_2O	36.0	2	23.84	14.33	7.2
c-$[O(CH_2)_2O(CH_2)_2]$	116.9	H_2O	28.0	2	26.18	14.57	9.4
CH_2O	133.4	Gas	53.2	11	17.17	13.84	1.8
CH_2O	133.4	H_2O	10.0	2	25.30	14.98	13.2
CH_3CHO	137.5	Gas	93.0	3	16.16	13.81	1.5
CH_3CHO	137.5	H_2O	7.3	1	24.36	14.99	13.2
CH_3COCH_3	108.7	Gas	93.0	3	16.16	13.81	−11.4
CH_3COCH_3	108.7	H_2O	1.1	4	27.79	14.50	−5.9
$CH_3COCH_2CH_3$	116.6	H_2O	9.0	1	19.86	13.68	−13.1
$(CH_3CH_2)_2CO$	116.6	H_2O	14.0	1	20.48	13.78	−12.3
$HCOOH$	98.6	H_2O	1.3	2	28.64	14.26	6.6
CH_3COOH	111.0	H_2O	0.16	3	30.85	14.96	−1.7
$CH_2(COOH)_2$	122.1	H_2O	0.2	2	29.29	15.13	0
$CH_3C(O)OCH_3$	108.7	Gas	1.6	2	26.86	14.38	6.6
$CH_3C(O)OCH_3$	108.7	H_2O	1.2	1	31.56	14.97	13.1
$CH_3C(O)OCH_2CH_3$	116.7	H_2O	4.0	1	27.57	14.76	11.1
$CH_3CH_2C(O)OCH_2CH_3$	116.7	H_2O	8.7	1	25.65	14.50	8.7
$[CH_3CH_2OC(O)CH_2]_2$	116.7	H_2O	7.8	1	27.64	14.77	11.2

The ΔE_μ row lists in brackets the % ΔE_μ in the total decrease in activation energy, which varies from 26 to 62 %, *i.e.* the contribution of the polar interaction of the reactive center O...H...C with a polar group is comparable to the decrease in the activation energy due to the change in the dissociation energy of the reacting C—H bond. The absolute value of ΔE_μ increases as the dipole moment of the functional group increase, and, probably, the electrostatic interaction contributes significantly to the decrease in activation energy. It is evident from the comparison of the changes of the relative values of r_e that the polar interaction causes the transition state to be more compact ($\Delta r_e < 0$). A reaction of the type:

$$HO^{\cdot} + RH \rightarrow H_2O + R^{\cdot}$$

was studied in the gas[6] and in the liquid[9] phases, which made it possible to compare of the polar effect in the two phases. The results of the calculation of br_e and ΔE_μ

Table 3. Kinetic parameters of the reactions of alkoxyl radicals with oxygen-containing compounds

RH	RO$^·$	Medium	$-\Delta H_e$ /kJ mol^{-1}	E_e /kJ mol^{-1}	br_e /(kJ mol^{-1})$^{1/2}$	ΔE_μ /kJ mol^{-1}	Number of measurements (n)
CH_4	$CH_3O^·$	Gas phase	8.5	57.2	14.05	0	1
C_4H_{10}	$(CH_3)_3CO^·$	Gas phase	40.7	42.2	13.90	0	1
CH_3OH	$CH_3O^·$	Gas phase	51.1	34.9	13.33	−6.6	1
CH_3OH	$CH_3O^·$	Liq. phase	45.3	39.5	13.62	0.7	2
CH_3OH	$(CH_3)_3CO^·$	Liq. phase	48.2	39.6	13.75	1.8	5
CH_3CH_2OH	$(CH_3)_3CO^·$	Liq. phase	51.5	35.4	13.36	−1.5	2
$CH_3(CH_2)_2OH$	$(CH_3)_3CO^·$	Liq. phase	51.5	35.2	13.35	−1.5	1
$(CH_3)_2CHOH$	$(CH_3)_3CO^·$	Liq. phase	61.8	32.0	13.36	−1.5	5
$(CH_3)_3COH$	$(CH_3)_3CO^·$	Liq. phase	25.6	50.6	14.02	4.4	1
c-$C_6H_{11}OH$	$(CH_3)_3CO^·$	Liq. phase	68.6	30.2	13.41	−1.1	3
$C_6H_5CH_2OH$	$(CH_3)_3CO^·$	Liq. phase	80.2	23.3	13.03	−8.8	2
$(C_6H_5)_2CHOH$	$(CH_3)_3CO^·$	Liq. phase	98.2	22.9	13.55	−4.5	3
$(C_6H_5)_2CHOH$	$C_6H_5CH_2O^·$	Liq. phase	94.5	21.2	13.17	−7.7	1
$(C_6H_5)_2CHOH$	*c*-$C_6H_{11}O^·$	Liq. phase	94.5	22.2	13.31	−6.5	1
$C_6H_5(CH_3)CHOH$	$(CH_3)_3CO^·$	Liq. phase	90.2	26.1	13.69	−3.4	1
CH_3COCH_3	$(CH_3)_3CO^·$	Gas phase	49.9	30.3	12.67	−17.8	1
CH_3COCH_3	$(CH_3)_3CO^·$	Liq. phase	49.9	34.1	13.17	−10.6	1
c-$C_6H_{10}O$	$(CH_3)_3CO^·$	Liq. phase	61.4	37.2	14.00	−3.6	3
$C_6H_5CH_2COCH_3$	$(CH_3)_3CO^·$	Liq. phase	87.9	27.7	13.82	−5.2	1
c-$C_6H_{11}COCH_3$	$(CH_3)_3CO^·$	Liq. phase	65.1	28.5	13.08	−11.3	1
CH_2O	$CH_3O^·$	Gas phase	77.5	32.0	14.03	0	1
CH_2O	$(CH_3)_3CO^·$	Gas phase	74.6	28.0	13.40	−4.2	1
CH_3CHO	$CH_3O^·$	Gas phase	81.6	20.2	12.56	−12.2	2
CH_3CHO	$(CH_3)_3CO^·$	Gas phase	78.7	27.8	13.53	−3.1	1
C_6H_5CHO	$CH_3O^·$	Liq. phase	94.5	12.4	11.76	−19.0	1
$(CH_3CH_2)_2O$	$(CH_3)_3CO^·$	Liq. phase	60.3	32.3	13.34	−1.7	4
$[(CH_3)_2CH]_2O$	$(CH_3)_3CO^·$	Liq. phase	70.6	32.7	13.81	2.3	1
$[(CH_3)_3C]_2O$	$(CH_3)_3CO^·$	Liq. phase	25.6	44.7	13.36	−1.5	1
$(CH_3)_3COCH_3$	$(CH_3)_3CO^·$	Liq. phase	55.0	39.0	13.96	3.5	2
$CH_2(OR)_2$	$(CH_3)_3CO^·$	Liq. phase	65.0	28.7	13.07	−3.9	8
$RCH(OR)_2$	$(CH_3)_3CO^·$	Liq. phase	84.8	26.8	13.50	−0.4	28
c-$[O(CH_2)_4]$	$(CH_3)_3CO^·$	Liq. phase	58.1	32.3	13.25	−2.4	3
c-$[O(CH_2)_5]$	$(CH_3)_3CO^·$	Liq. phase	65.0	33.5	13.71	1.4	2
c-$[OCH(OR)(CH_2)_n]$	$(CH_3)_3CO^·$	Liq. phase	84.8	26.9	13.62	0.6	5
c-$[OCH(R)O(CH_2)_n]$	$(CH_3)_3CO^·$	Liq. phase	84.8	26.3	13.52	−0.2	7
c-$[OCH(R)O(CH_2)_n]$	*c*-$C_6H_{11}O^·$	Liq. phase	83.1	29.8	13.92	3.2	1
c-$[OCH_2O(CH_2)_n]$	$(CH_3)_3CO^·$	Liq. phase	65.0	13.2	13.47	−0.6	6
c-$[OCH_2O(CH_2)_5]$	*c*-$C_6H_{11}O^·$	Liq. phase	63.3	33.6	13.64	0.8	1
$HC(O)OCH_3$	$(CH_3)_3CO^·$	Liq. phase	37.3	34.8	12.65	−7.2	1
$CH_3C(O)OCH_2CH_3$	$(CH_3)_3CO^·$	Liq. phase	57.9	42.3	14.47	8.0	1
$CH_3C(O)OC_6H_5$	$(CH_3)_3CO^·$	Liq. phase	47.0	39.9	13.74	1.7	2
c-$C_6H_{11}OC(O)CH_3$	$(CH_3)_3CO^·$	Liq. phase	57.1	29.2	12.79	−6.1	3
$(C(O)OCH_3)_2$	$(CH_3)_3CO^·$	Liq. phase	49.9	44.9	14.45	7.8	1
$C_6H_5CH_2C(O)OCH_3$	$(CH_3)_3CO^·$	Liq. phase	66.0	29.2	13.17	−3.1	1
$C_6H_5C(O)OCH_3$	$(CH_3)_3CO^·$	Liq. phase	49.9	43.4	14.28	6.3	1
$C_6H_5C(O)OCH_2C_6H_5$	$(CH_3)_3CO^·$	Liq. phase	87.9	27.3	13.77	−2.7	1

are given in Table 2. The activation energy was calculated using the value of the reaction rate constant k, in this case the pre-exponential factor $A = 4 \cdot 10^9$ L mol^{-1} s^{-1} for reactions with the C—H bond of aliphatic compounds, and $A = 4 \cdot 10^8$ L mol^{-1} s^{-1} for reactions with olefins, ketones, alkylaromatic compounds and acids (the C—H bond of the acid residue). In the liquid phase the collision rate of the reagents is higher due to the small free volume and, as a result, the pre-exponential factor was multiplied by a coefficient equal to 5 (see Ref. 10), $A_{lph} = 5A_{gph}/ = 2 \cdot 10^{10}$ L mol^{-1} s^{-1}) for the reaction of HO· with one aliphatic C—H bond. The coefficient α for this reaction is equal to $(b_i/b_f) = 0.79$.

As can be seen from the results given in Table 2, the reactions of hydroxyl with paraffin hydrocarbons of various structures in the gas and liquid phases are characterized by the same parameter, $br_e = 13.58 \pm 0.17$ (kJ mol^{-1})$^{1/2}$, for reactions of OH with toluene $br_e = 15.08$, and with cyclohexane $br_e = 15.14$. The ΔE_μ value for some reactions is more than zero, for others less than

Table 4. Contribution of the polar effect (ΔE_μ) to the activation energy of reactions of radicals having a free valence on oxygen with oxygen-containing compounds in the gas phase

RH	ΔE_μ			
	O	$HO^\cdot$	$CH_3O^\cdot$	$(CH_3)_3CO^\cdot$
CH_3OH	4.6	2.4	−6.0	—
$(CH_3)_2CHOH$	−8.8	−1.3	—	—
CH_2O	−4.6	1.8	0	−4.2
RCHO	−7.9	1.5	−12.2	−3.1
CH_3COCH_3	−9.4	−11.4	—	−17.8
$R'CH_2COR''$	−15.6	−9.3	—	—
$(CH_3)_2O$	−5.1	2.8	—	—
$R'CH_2OR''$	−6.7	−1.4	—	—
CH_3COOCH_2R'	0	6.6	—	—

Table 5. The effect of solvation and its contribution ΔE_{solv} to the activation energy of the $HO^\cdot(RO^\cdot)$ + RH reaction

RH	$\Delta E_\mu{}^a$ (Gas phase)	$\Delta E_\mu{}^a$ (Liq. phase)	$\Delta E_{solv}{}^a$
CH_3OH	2.4	6.6	4.2
CH_3CH_2OH	−1.3	4.4	5.7
$(CH_3)_2CHOH$	−2.7	5.3	8.0
$(CH_3)_3COH$	−2.0	5.4	7.4
CH_3OCH_3	2.8	10.6	7.8
$(CH_3CH_2)_2O$	−1.4	7.2	8.6
CH_2O	1.8	13.2	11.4
CH_3CHO	1.5	13.2	11.7
CH_3COCH_3	−11.4	−5.9	5.5
CH_3COOCH_3	6.6	13.1	6.5
CH_3OH^b	−6.0	0.7	6.7
$CH_3COCH_3{}^c$	−17.8	−10.6	7.2

[a] Values are given in kJ mol^{-1}. [b] Reaction with $CH_3O^\cdot$, CH_3OH (Liq. phase). [c] Reaction with $(CH_3)_3CO^\cdot$, CH_3COCH_3 (Liq. phase).

zero (see Table 2), *i.e.*, polar interaction in some cases results in a decrease and in other cases in an increase in the activation energy of the reaction. The strongest effect of the polar interaction is felt in the attack of hydroxyl on ketones and aldehydes.

The effect of multidipole interaction [11] and its dependence on the distance between the alcohol groups (where the weaker C—H bond is attacked) can be seen from a comparison of ΔE_μ for diols in H_2O. The more methyl groups separating the two alcohol groups, the smaller ΔE_μ (kJ mol^{-1}):

RH	ΔE_μ
$CH_3(CHOH)_2CH_3$	8.6
$CH_2OH(CH_2)_2CH_2OH$	4.9
$CH_2OH(CH_2)_3CH_2OH$	4.5

The analysis of kinetic data on the reactions of alkoxyl radicals with hydrocarbons has been analyzed previously.[12] In this work we calculated br_e for the reactions of alkoxyl radicals with oxygen-containing compounds in the liquid phase as well as in the gas phase. The rate constants were taken from Refs. 6, 13, the energies of the bond dissociation — from Refs. 7, 8. Coefficient $\alpha = (b_i/b_f) = 0.80$ (see Ref. 12). The pre-exponential factor A for the reaction of $RO^\cdot$ with one C—H bond of an aliphatic compound in the liquid phase amounts 10^9 L mol^{-1} s^{-1}, while that in the gas phase is as high as 2×10^8; for the reactions of $RO^\cdot$ with unsaturated, alkylaromatic compounds, ketones, acids and esters (acid residue) A was less by a factor of 10. It follows from the data of Table 3 that the polar interaction significantly decreases the activation barrier in reactions of $RO^\cdot$ with ketones (comparison parameter $br_{eRH} = 14.41$), with aldehydes ($br_{eRH} = 13.54$), and with aromatic alcohols ($br_{eRH} = 14.08$). The polar interaction has little effect on the activation energy of the reactions of aliphatic alcohols, ethers, acetals, and cyclic ethers ($br_{eRH} = 13.54$).

It is appropriate to compare the value of the polar effect in reactions of the radicals having a free valence on oxygen with different classes of organic compounds, and average the value of the activation energy for structurally similar compounds in Table 4.

As can be seen from the results given in Table 4, the contribution of the polar effect to the activation energy can be positive or negative depending on the radical (atom) attacking the polar molecule as well as on the functional group in the reagent molecule; in some cases, the contribution is equal to zero. It is observed to be most efficient in the reactions of radicals with ketones and aldehydes. The contribution of the polar interaction differs in the gas and liquid phases for the same reaction (see Tables 3, 4). Since both the transition state and the reagents are solvated in polar solvents (water), this difference should be explained by the superposition of two effects in the liquid phase: polar interaction and solvation. It is possible to estimate the contribution of solvation to activation energy ΔE_{solv} by comparing ΔE_μ for these two phases and defining it as the difference $\Delta E_{solv} = (\Delta E)_{lph} - (\Delta E)_{gph}$. From a comparison of ΔE_μ in the gas and liquid phases it follows (Table 5) that the transfer of the reaction from the gas phase into the liquid phase in all cases is accompanied by an increase in the activation energy, and ΔE_{solv} ranges from 4 to 11 kJ mol^{-1} s^{-1}; the maximum value is observed for the reaction of hydroxyl with aldehydes. For the reaction of hydroxyl with hydrocarbons, as indicated earlier, br_e in the gas and liquid phases are close, and $\Delta E_{solv} = 0\pm0.15$ kJ mol^{-1}. Apparently, the difference between the solvation energies of the attacking molecule and the transition state makes the main contributes to ΔE_{solv}.

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