Polar Effect and Geometry of the Transition State in the Reactions of Ozone with C–H Bonds of Polar Molecules

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Abstract—A large body of experimental data on the reactions of ozone with C–H bonds of polar molecules in the liquid and gas phases is analyzed in the framework of the intersecting parabolas model. The reactions are considered as the abstraction reaction $O_3 + RH \longrightarrow HOOO^{\bullet} + R^{\bullet}$. The contribution from the polar effect to the activation energy of such reactions is calculated. This contribution is –6.8 kJ/mol for the reactions of ozone with aliphatic alcohols, and is –8.1, –11.7, –6.8, and –2.2 kJ/mol for the reactions of ozone with ketones, ethers, 1,3-dioxolanes, and 1,3-dioxanes, respectively. The contribution is insignificant in the reactions of ozone with aldehydes. The interatomic distances in the transition state of these reactions $r^{\#}(C{\ldots}H)$ and $r^{\#}(O{\ldots}H)$ and the angle between the C…H and O…H bonds are calculated. For the reactions in polar solvents, the contribution from solvation to the activation energy is calculated. In most of the systems considered, this contribution is insignificant (from –1 to –3 kJ/mol). The reactions involving ozone are compared to the reactions of peroxy radicals with the same classes of compounds.

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INTRODUCTION

The reactions of ozone with aliphatic compounds have been studied rather well experimentally [1–3]. Radical formation in these reactions has been proved [2, 4]. The most substantiated primary elementary act of the reactions of ozone with aliphatic compounds is the abstraction reaction [5]

$$O_3 + RH \longrightarrow HOOO^{\bullet} + R^{\bullet}.$$
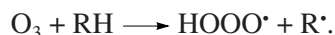
In our earlier work [5], the reactions of ozone with hydrocarbons were analyzed in the framework of the intersecting parabolas model (IPM). The analysis showed that the following factors make an important contribution to the activation energy in addition to the reaction enthalpy: the triplet repulsion in the transition state (TS), the interaction of electrons of the TS with adjacent π electrons, the difference in the electronegativity of atoms of the reaction center of the TS, and the force constants of the breaking and forming bonds. One more factor is pronounced in the reactions of peroxy radicals with polar organic compounds, namely, the polar interaction of the reaction center with the polar group of a molecule [4, 5–9]. Since ozone is a polar compound (its dipole moment is 0.534 D [10]) and the TS of the reactions of ozone with the C–H bond of an organic compound is unambiguously polar, the appearance of the polar interaction should be expected in these reactions. They have been studied experimentally, and a large body of experimental data on these reactions is available [11, 12]. The purpose of the present work is to estimate the contribution from the polar interaction to the activation energy of the reactions of ozone with saturated polar compounds in which the weakest C–H bonds are attacked. As in an earlier study [5], the IPM was used as the method of investigation.

COMPUTATIONAL METHOD

In the IPM, the energy profile of the reaction of the type

$$O_3 + RH \longrightarrow [OOO{\ldots}H{\ldots}R]^{\#} \longrightarrow HOOO^{\bullet} + R^{\bullet}$$

is approximated by two parabolas. One of them describes the stretching vibration of the attacked C–H bond, and the other describes that of the forming O–H bond. All elementary reactions can be classified according to the atomic structure of the TS, the force constants of the bonds involved in rearrangement, and the distance between the vertices of the intersecting parabolas. The IPM makes it possible to calculate the activation energy from parameters derived from experimental data, and the rate constant of the abstraction reaction can be calculated from its enthalpy ΔH.

The elementary abstraction reaction is characterized in the IPM by the following parameters [4, 5, 13–15].

(1) The classical enthalpy ΔH_e, including the reaction enthalpy and zero-point energies of the reacting bonds. In turn, the enthalpy of this reaction is equal to the difference of the dissociation energies of the breaking and forming bonds: $\Delta H = D_{C–H} - D_{O–H}$. The strengths of the C–H bonds of polar molecules were borrowed from [16, 17]. The dissociation energy of the

O–H bond in the hydrotrioxide HOOO⋅ radical is $D_{O-H} = 350.4$ kJ/mol [5], and the difference in the zero-point vibration energies of the reacting bonds is $0.5hN_A(\nu_{C-H} - \nu_{H-O}) = -3.8$ kJ/mol. Therefore, as applied to the reaction considered,

$$\Delta H_e = \Delta H + 0.5hN_A(\nu_{C-H} - \nu_{O-H})$$
$$= D_{C-H} - 354.2 \text{ kJ/mol}, \tag{1}$$

where h is Planck's constant, N_A is Avogadro's number, and ν is the stretching frequency of the corresponding bond.

(2) The classical potential barrier E_e, which is related to the Arrhenius activation energy E by the equation

$$E_e = E + 0.5hN_A\nu_{C-H} - 0.5RT, \tag{2}$$

where $E = RT\ln(nA/k)$, A is the preexponential factor, n is the number of equireactive C–H bonds in the molecule, and k is the reaction rate constant.

The zero-point vibration energy of the C–H bond is equal to 17.4 kJ/mol [13]. Particular values of the enthalpy and activation energy characterize an individual reaction. The calculation of E_e from experimental data is performed using the formula

$$E_e \text{ (kJ/mol)} = RT\ln(nA/k) + 17.4 - 0.5RT. \tag{3}$$

(3) The coefficients b_{C-H} and b_{O-H} and the coefficient $\alpha = b_{C-H}/b_{O-H} = 0.814$, where $b_{C-H} = 2\pi\nu_{C-H}\mu_{C-H}^{1/2} = 3.743 \times 10^{11}$ (kJ/mol)$^{1/2}$ m^{-1}, $b_{O-H} = 2\pi\nu_{O-H}\mu_{O-H}^{1/2} = 4.600 \times 10^{11}$ (kJ/mol)$^{1/2}$ m^{-1} (μ is the reduced mass of atoms forming the bond).

(4) The parameter r_e, which is the total extension of the C–H and O–H bonds in the TS, $r_e = \Delta r_{C-H}^{\#} + \Delta r_{O-H}^{\#}$.

(5) The preexponential factor A and the number n of the equireactive C–H bonds that are attacked by ozone. The last three parameters are characteristics of the whole class of reactions. For the reaction of ozone with one C–H bond, $A = 2 \times 10^9$ l mol^{-1} s^{-1} [15].

The parameter br_e is calculated from experimental kinetic data using the following formula:

$$br_e = \alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e}. \tag{4}$$

This parameter characterizes the whole class of reactions and makes it possible to calculate the classical potential barrier $E_{e,0}$ of the thermally neutral reaction ($\Delta H_e = 0$) [13].

$$E_{e,0} = (br_e)^2/(1 + \alpha)^2. \tag{5}$$

If α and br_e are known, then, knowing the reaction enthalpy, the activation energy of the reaction can be calculated by the formulas ($B = br_e/(1 - \alpha^2)$) [13]

$$\sqrt{E_e} = B\left\{1 - \alpha\sqrt{1 - \frac{\Delta H_e}{Bbr_e}}\right\}, \tag{6}$$

$$E = E_e - 17.4 + 0.5RT, \tag{7}$$

and the rate constant can be calculated using the Arrhenius formula

$$k = nA\exp(-E/RT). \tag{8}$$

Polar effect. If the molecule attacked by ozone contains a polar group, then the polar interaction between this group and the reaction center of the TS occurs in the TS. This interaction affects the activation energy. The contribution from the interaction to the activation energy can be estimated in the framework of the IPM as follows [6]. All aliphatic hydrocarbons reacting with ozone are characterized by the same parameter $br_{e,0} = 13.62$ (kJ/mol)$^{1/2}$, and, for the reactions of alkylaromatic hydrocarbons, $br_{e,0} = 14.32$ (kJ/mol)$^{1/2}$ [15]. The appearance of the polar group changes the activation energy by adding the increment ΔE_μ. This increment is estimated from the formula [6]

$$\Delta E_\mu = \frac{(br_e)^2 - (br_{e,0})^2}{(1 + \alpha)^2}, \tag{9}$$

where br_e characterizes the reaction of the polar compound with ozone in the gas phase or in a nonpolar solvent and $br_{e,0}$ refers to the reaction of ozone with the C–H bond of hydrocarbon.

Solvation effect. The reactions of polar species are also characterized by the solvation effect modifying the rate and activation energy of the process. The contribution from solvation to the activation energy can be characterized by the increment ΔE_s. This parameter can also be estimated as the polar effect by comparing the br_e parameters in the polar ($br_{e,s}$) and nonpolar (br_e) solvents. The formula for the estimation of the ΔE_s increment is similar to that the formula for the estimation of the polar effect and has the following form (CCl$_4$ is a nonpolar solvent) [8]:

$$\Delta E_s = \Delta E_{\mu,s}(\text{solv.}) - \Delta E_\mu(\text{CCl}_4). \tag{10}$$

TS geometry. Combining the IPM with quantum chemical calculations allowed us to calculate the geometry of the TS for the abstraction reactions from the ΔH and E values [18]. In the reaction of ozone with the C–H bond of a hydrocarbon, as in the reaction of the peroxy radical, the reaction center of the TS has a linear configuration (the C, H, and O atoms lie in one line) [19]. In the reaction between ozone and a C–H bond of a polar compound, as in the similar reaction of the peroxyl radical, the reaction center of the TS in the case of $\Delta E_\mu < 0$ has an angular configuration and is additionally characterized by a $\varphi = \varphi(C…H…O)$ angle [19].

$$r_{RH}^{\#}(C…H) \qquad r_{RH}^{\#}(O…H)$$

$$r_\mu^{\#}(C…O)$$
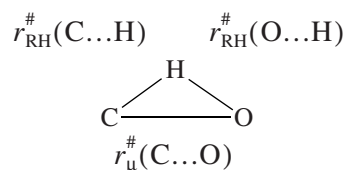
In this reaction center, the $r_{RH}^{\#}(C…H)$ and $r_{RH}^{\#}(O…H)$ distances are the same as in the reaction between the hydrocarbon and O$_3$ with the equivalent enthalpy

$(\Delta H_\mu = \Delta H_{RH})$, and the $r_\mu^{\#}(C...O)$ distance is characteristic of the reaction with a polar compound.

To estimate the geometric parameters in the case of such reactions, one should know ΔH, E, and the activation energy of the reaction with hydrocarbon (E_{RH}) with the same D_{C-H}. As was mentioned above, $E_{RH} = E - \Delta E_\mu$. The formulas for the calculation of the geometric parameters, namely, the C...H and O...H distances and the $\varphi(C...H...O)$ angle, have the form [18, 19]

$$r^{\#}(C–H) = r(C–H) + \beta b_{C-H}^{-1}\sqrt{E_e - \Delta E_\mu}, \quad (11)$$

$$r^{\#}(O...H) = r(O–H) + \alpha\beta b_{C-H}^{-1}\sqrt{E_e - \Delta E_\mu - \Delta H_e}, (12)$$

$$r_\mu^{\#}(C...O) = r(C–H) + r(O–H) \\ + \beta b_{C-H}^{-1}\sqrt{E_e} + \alpha\beta b_{O-H}^{-1}\sqrt{E_e - \Delta H_e}, \quad (13)$$

$$\cos(180° - \varphi) \\ = \frac{r_\mu^{\#}(C...O)^2 - r^{\#}(C...H)^2 - r^{\#}(O...H)^2}{2r^{\#}(C...H)r^{\#}(O...H)}, \quad (14)$$

where $r^{\#}(C...H)$ and $r^{\#}(O...H)$ are the interatomic distances in the TS of the reaction $O_3 + RH$ and $r_\mu^{\#}(C...O)$ is the C–O distance in the TS of the reaction of ozone with the polar compound $R_\mu H$. The C–H bond length is $r(C–H) = 1.092 \times 10^{-10}$ m [10], and the O–H bond length in the HOOO$^\bullet$ radical is $r(O–H) = 0.970 \times 10^{-10}$ m (as in a hydroperoxide molecule [4]). The proportionality coefficient β between the bond extension according to the quantum-chemical calculation and IPM is as follows:

$$\beta = [r^{\#}(C...O)_{quant.-chem} \\ - r(C–O)_{quant.-chem}]/\Delta r^{\#}(C...O)_{IPM} = 1.437. \quad (15)$$
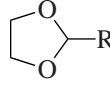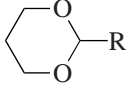
RESULTS AND DISCUSSION

Polar effect. The polar effect in the reactions of ozone with polar molecules can be estimated from the kinetic characteristics (rate constant and activation energy) of the reactions of ozone in the gas phase and in a nonpolar solvent (heptane, CCl$_4$). The initial data (reaction enthalpies and activation energies) and the results of calculation of br_e are given in Table 1 [20–34].

The tabulated data show that the majority of oxygen-containing compounds reacting with ozone have an individual parameter br_e different from the parameters $br_{e, 0} = 13.62$ (kJ/mol)$^{1/2}$ and $br_{e, 0} = 14.32$ (kJ/mol)$^{1/2}$, which are characteristic of saturated and alkylaromatic hydrocarbons, respectively [15]. For ketones, the role of the reference is played by the unsaturated compounds, for which $br_{e, 0} = 15.21$ (kJ/mol)$^{1/2}$ [15]. The only exception is one class of compounds, namely, aliphatic aldehydes, whose reactions with ozone have a br_e parameter

close to $br_{e, 0} = 13.62$ (kJ/mol)$^{1/2}$, whereas in the reaction of benzaldehyde it is close to $br_{e, 0} = 14.32$ (kJ/mol)$^{1/2}$, which is characteristic of alkylaromatic hydrocarbons. For the great majority of compounds $br_e < br_{e, 0}$, which implies that, for these reactions, the polar effect reduces the activation energy. The ΔE_μ increments calculated using formula (8) are given in Table 2.

An analysis of the obtained data suggests that the functional group is decisive in the polar interaction. Depending on the class of organic compounds, the ΔE_μ increments (kJ/mol) are arranged as follows:

Class of compounds	$\Delta E_\mu(O_3)$, kJ/mol	φ, deg	$\Delta E_\mu(RO_2^\bullet)$, kJ/mol
ROR	-11.7 ± 1.6	155 ± 0.7	-2.9 ± 1.3
cyclo-[(CH$_2$)$_n$O	-10.6 ± 0.2	157 ± 0.1	$-$
RC(O)R	-8.1 ± 1.1	161 ± 0.5	-7.6 ± 2.2
ROH	-6.8 ± 0.6	162 ± 0.3	-7.5 ± 1.4
(5-membered cyclic acetal)–R	-6.8 ± 1.2	162 ± 0.5	-4.2 ± 0.5
(6-membered cyclic acetal)–R	-2.2 ± 0.2	170 ± 0.1	-3.5
RCH(O)	-0.1 ± 1.0	176 ± 0.4	-5.6 ± 1.1

The transition state of the reaction of ozone with the C–H bond (C...H...O) is close to that for the reaction of the peroxy radical. The polar effect in the reactions of $RO_2^\bullet$ with the oxygen-containing compounds has been studied earlier [4, 6–9]. Therefore the increments ΔE_μ for the reactions of $RO_2^\bullet$ and O_3 with compounds of different classes are compared in the above table. The comparison shows that the ΔE_μ increments are similar for the reactions of ozone and peroxy radicals with alcohols, ketones, and cyclic acetals, whereas they differ substantially for the reactions with aldehydes and ethers.

The geometric parameters of the TS for the reactions under study are given in Table 2. A linear correlation is observed between the values of $|\cos(180° - \varphi)|$ and ΔE_μ (Fig. 1). This correlation has the following analytical expression valid for $\Delta E_\mu < 1$:

$$\cos(180° - \varphi) = 1.00 + 7.60 \times 10^{-3}\Delta E_\mu(kJ/mol). \quad (16)$$

The $r^{\#}(C...H)$ interatomic distance in the TS elongates with an increase in the reaction enthalpy. This dependence is linear (Fig. 2) and is described for aliphatic compounds by the following analytical expression:

$$r^{\#}(C...H) \times 10^{10} \text{ (m)} \\ = 1.375 + 1.21 \times 10^{-3}\Delta H \text{ (kJ/mol)}. \quad (17)$$

Table 1. Activation energies and br_e parameters calculated using formula (4) for reactions of O_3 with compounds containing functional groups in the nonpolar solvent CCl_4
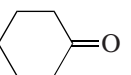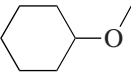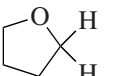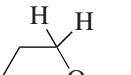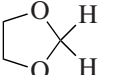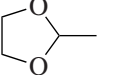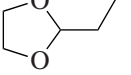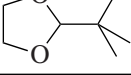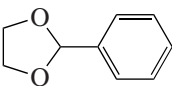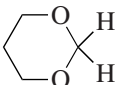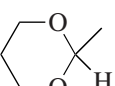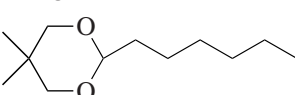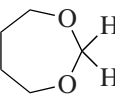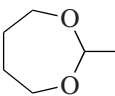
Reactants	ΔH, kJ/mol	E, kJ/mol	br_e, $(kJ/mol)^{1/2}$	Literature
CH_3OH	60.6	63.4 ± 1.4	12.81 ± 0.20	[20, 21]
$MeCH_2OH$	49.4	57.7 ± 0.2	12.92 ± 0.02	[20, 22–24]
$EtCH_2OH$	49.1	55.6 ± 0.8	12.66 ± 0.10	[20, 21]
$PrCH_2OH$	49.1	56.2 ± 0.7	12.73 ± 0.07	[21, 24]
Me_2CHCH_2OH	49.1	55.8	12.69	[20]
Me_2CHOH	40.1	52.0 ± 1.6	12.85 ± 0.20	[20, 21, 24]
$EtMeCHOH$	40.1	52.1 ± 0.2	12.86 ± 0.02	[20, 24]
cyclohexanol (structure with H, OH)	38.0	50.0 ± 0.2	12.73 ± 0.02	[2, 21]
$MeCH(O)$	23.4	48.8 ± 3.5[1]	13.53 ± 0.42	[20, 25][1]
$Me_3CCH(O)$	24.7	41.0	13.59	[26]
$PhCH_2CH(O)$	11.6	45.5	13.82	[26]
$Me_2CH(Me)C(O)$	12.2	50.1	14.33	[27][1]
$PhCH(O)$	–2.4	46.0	14.62	[28]
$MeCH_2C(O)Me$	42.2	64.3	14.25	[29]
cyclohexanone (structure =O)	43.7	62.7 ± 1.5	14.00 ± 0.17	[24, 31]
Et_2O	49.1	52.4 ± 0.4	12.21 ± 0.06	[26, 32]
Pr_2O	49.1	51.2	12.04	[32]
Bu_2O	49.1	50.2	11.89	[26]
$(BuCH_2)_2O$	49.1	50.7	11.96	[32]
$(MeOCH_2)_2$	49.1	55.7	12.67	[26]
$(ClCH_2CH_2)_2O$	49.1	63.1 ± 0.9	13.54 ± 0.11	[26, 32]
$Me_2CHOCHMe_2$	40.4	49.9	12.55	[32]
$(Me_2CHCH_2CH_2)_2O$	49.1	50.7	11.96	[32]
cyclohexyl methyl ether (structure)	37.2	51.9	13.05	[1]
tetrahydrofuran (structure, O, H, H)	41.2	48.6	12.30	[26]
tetrahydropyran (structure, H, H, O)	51.3	53.8	12.23	[26]
1,3-dioxolane (structure, O, O, H, H)	30.8	46.1 ± 0.6	12.73 ± 0.07	[26, 33]
2-methyl-1,3-dioxolane (structure, O, O)	23.0	45.1 ± 0.3	13.10 ± 0.04	[33, 34]
2-ethyl-1,3-dioxolane (structure, O, O)	22.1	42.6	12.85	[33]
2-tert-butyl-1,3-dioxolane (structure, O, O)	22.7	41.0	12.60	[33]

Table 1. (Contd.)

Reactants	ΔH, kJ/mol	E, kJ/mol	br_e, $(kJ/mol)^{1/2}$	Literature
	22.7	42.1	12.75	[33]
	22.1	41.3	12.68	[33]
	37.6	55.0	13.42	[34]
	27.6	48.8	13.28	[34]
	28.5	42.7	12.43	[33][2]
	55.3	62.2	13.08	[26]
	35.1	50.9	13.07	[34]
	30.4	47.0	12.88	[34]

[1] Gas phase.
[2] Hexane.

Solvation effect. In a polar solvent, both the oxidized molecule and ozone and the TS are solvated. Therefore, the solvation effect should be observed for the considered systems in addition to the polar effect.

Its contribution to the activation energy can be estimated by comparing the br_e and ΔE_μ parameters calculated by the experimental data. The latter parameter for the reaction in a polar solvent includes both the polar
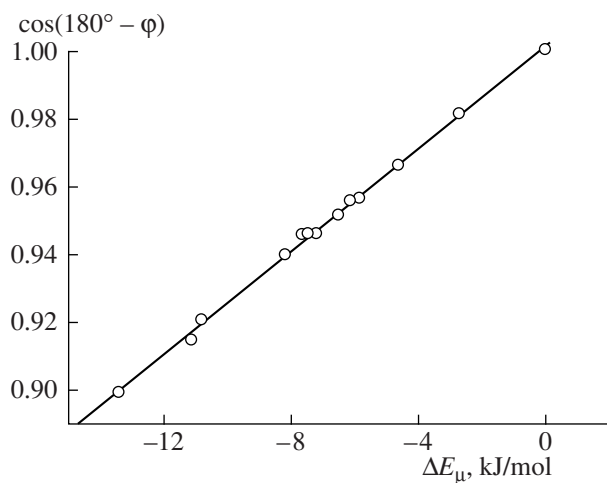
Fig. 1. Correlation of $\cos(180° - \varphi)$ with the contribution from the polar interaction ΔE_μ to the activation energy of the reactions of ozone with aliphatic compounds.
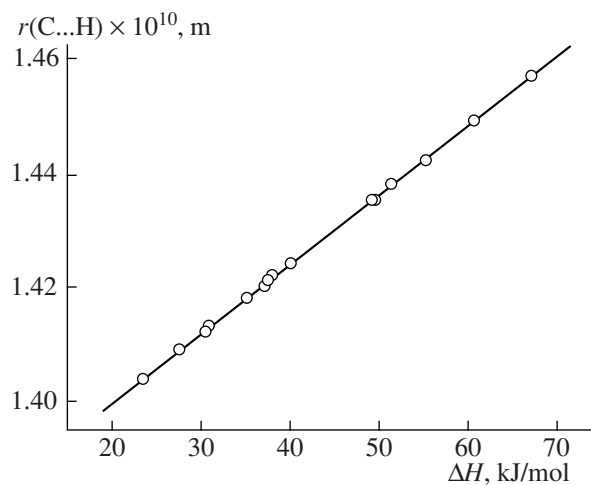
Fig. 2. Dependence of the interatomic distance in the TS of the reactions of ozone with aliphatic compounds on the reaction enthalpy.

Table 2. Contribution from the polar interaction ΔE_{μ} to the activation energy and geometric parameters of the TS of reactions of O_3 with compounds containing functional groups (the kinetic parameters necessary for the calculation were taken from Table 1)
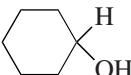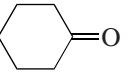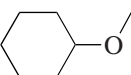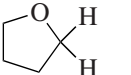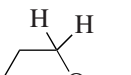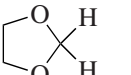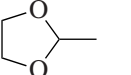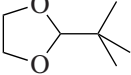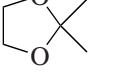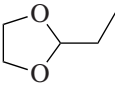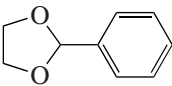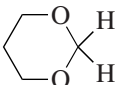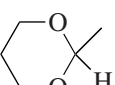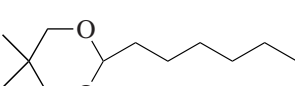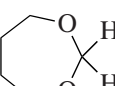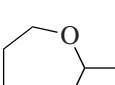
Reactants	ΔE_{μ}, kJ/mol	$r^{\#}(C{\dots}H) \times 10^{10}$, m	$r^{\#}(O{\dots}H) \times 10^{10}$, m	φ, deg
CH_3OH	−6.5	1.449	1.137	162
$MeCH_2OH$	−5.8	1.435	1.151	163
$EtCH_2OH$	−7.7	1.435	1.151	161
$PrCH_2OH$	−7.2	1.435	1.151	161
Me_2CHCH_2OH	−7.5	1.435	1.151	161
Me_2CHOH	−6.2	1.424	1.162	163
$EtMeCHOH$	−6.1	1.424	1.162	163
cyclohexanol (C$_6$H$_{11}$, H, OH)	−7.2	1.422	1.164	161
$MeCH(O)$	−0.8	1.404	1.182	174
$Me_3CCH(O)$	−0.3	1.384	1.202	177
$PhCH_2CH(O)$	1.6	1.390	1.196	180
$PhCH(O)$	2.6	1.389	1.197	180
$MeCH_2C(O)Me$	−8.5	1.455	1.131	160
$Me_2CHC(O)Me$	−7.8	1.424	1.162	161
cyclohexanone (ring=O)	−10.6	1.457	1.129	163
Et_2O	−11.1	1.436	1.150	156
Pr_2O	−12.3	1.436	1.150	155
Bu_2O	−13.4	1.436	1.150	154
$(BuCH_2)_2O$	−12.9	1.436	1.150	154
$(MeOCH_2)_2$	−7.6	1.435	1.151	161
$(ClCH_2CH_2)_2O$	−0.7	1.436	1.150	178
$Me_2CHOCHMe_2$	−8.5	1.425	1.161	160
$(Me_2CHCH_2CH_2)_2O$	−12.9	1.436	1.150	154
cyclohexyl–O– (ether)	−4.6	1.420	1.166	165
tetrahydrofuran (O ring, H H)	−10.4	1.426	1.160	157
tetrahydropyran (O ring, H H)	−10.9	1.438	1.148	157
1,3-dioxolane (O, O ring, H H)	−7.2	1.413	1.173	161
2-methyl-1,3-dioxolane (O, O ring)	−4.2	1.404	1.182	166
2-tert-butyl-1,3-dioxolane (O, O ring)	−8.2	1.403	1.183	160
2,2-dimethyl-1,3-dioxolane (O, O ring)	−7.0	1.403	1.183	162

Table 2. (Contd.)

Reactants	ΔE_μ, kJ/mol	$r^{\#}(\text{C}\ldots\text{H}) \times 10^{10}$, m	$r^{\#}(\text{O}\ldots\text{H}) \times 10^{10}$, m	φ, deg
[structure]	−6.2	1.402	1.184	163
[structure]	−13.3	1.424	1.188	155
[structure]	−1.7	1.421	1.165	171
[structure]	−2.8	1.409	1.177	169
[structure]	−9.4	1.410	1.176	158
[structure]	−4.4	1.442	1.144	166
[structure]	−4.5	1.418	1.168	165
[structure]	−6.0	1.412	1.174	163

Note: The $\varphi(\text{C}\ldots\text{H}\ldots\text{O})$ angle for the TS.

and solvation effects. They can be separated using formula (10). The initial data (ΔH and E) and the br_e parameters calculated from them (formula (4)) are presented in Table 3 [2, 20, 22, 26, 33, 35–44]. The ΔE_s increments calculated using the data from Table 1 and Table 3 are given in Table 4.

It can be seen that, for most of the reactions studied, solvation reduces the activation energy of the reactions of ozone with polar compounds. However, its effect is low: even in such a polar solvent as water (dielectric constant $\varepsilon = 80$), the contribution from solvation to the activation energy of the reactions of ozone with alcohols is only $\Delta E_{\mu, av} = -0.8$ kJ/mol. A similar situation is observed for the oxidation of other compounds. In these cases, evidently, the solvation energy for the TS is close to that for the initial reactants. The same regularity is observed for the reactions of peroxyl radicals with hydrocarbons and ketones in polar solvents [45].

In the case of oxidation of methyl ethyl ketone, diethyl ether, and others, the activation energy increases in a polar solvent. It is most likely that in these reactions the TS is solvated to a lesser extent than the starting reactant.

For many reactions the rate constants were measured only in the polar solvent. In such cases, the polar and solvation effect cannot be separated. The results of calculation of the sum of increments $\Delta E_\mu + \Delta E_s$ from the experimental data are presented in Table 5.

It can be seen that this total increment varies in a wide range from −26 to 6 kJ/mol and is negative in all but six reactions.

Since the TS of the reactions of ozone and $RO_2^{\bullet}$ with C–H bonds are similar, it is reasonable to compare ΔE_s of these two classes of reactions. For this purpose, we calculated the br_e parameters for the reactions of $RO_2^{\bullet}$ with methanol and acetaldehyde in the gas and liquid phases using the experimental data by the formula

$$\Delta E_s = \frac{[br_e(\text{solv})]^2 - [br_e(\text{gas})]^2}{(1 + \alpha)^2} \quad (18)$$

and calculated the contribution from the solvation to the activation energy. The results of this calculation are presented below.

Table 3. Activation energies and br_e parameters calculated using formula (4) for reactions of O_3 with compounds containing functional groups in polar solvents
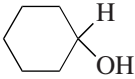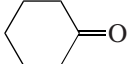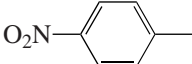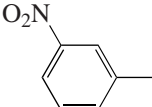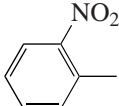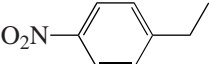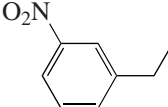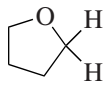
Reactants	Solvent	ΔH, kJ/mol	E, kJ/mol	br_e, $(kJ/mol)^{1/2}$	Reference
CH_3OH	H_2O	60.6	63.7 ± 0.7	12.85 ± 0.15	[20, 35]
$MeCH_2OH$	CH_2ClCH_2Cl	49.4	56.0	12.70	[22]
$MeCH_2OH$	AcOH	49.4	57.6	12.92	[22]
$MeCH_2OH$	H_2O	49.4	55.2 ± 1.1	12.58 ± 0.15	[20, 35, 36]
$EtCH_2OH$	H_2O	49.1	55.8 ± 0.5	12.69 ± 0.07	[20, 35]
$PrCH_2OH$	H_2O	49.1	55.8	12.68	[35]
$Me(CH_2)_7OH$	H_2O	49.1	54.4	12.50	[35]
Me_2CHOH	H_2O	40.1	50.3 ± 0.3	12.63 ± 0.04	[20, 35]
cyclohexanol (C$_6$H$_{11}$, H, OH)	H_2O	38.0	50.5	12.80	[2]
CH_2OHCH_2OH	H_2O	51.1	58.9	12.96	[37]
$MeCH(O)$	H_2O	23.4	51.2	13.84	[35]
$CH_2OH(CHOH)_4CH(O)$	H_2O	21.0	54.1	14.32	[35]
$PhCH(O)$	H_2O	–2.4	50.5	15.11	[35]
$CH_3C(O)OH$	AcOH	63.7	55.9	11.34	[38]
$MeCH_2C(O)Me$	H_2O	42.2	67.5 ± 3.8	14.52 ± 0.42	[35, 39, 40]
cyclohexanone (C$_6$H$_{10}$=O)	H_2O	43.7	66.2	14.38	[40]
$CHCl_3$	H_2O	46.7	57.8	13.14	[35]
$CHBr_3$	H_2O	48.8	62.3	13.58	[35]
CH_2Cl_2	H_2O	56.3	59.5	12.62	[35]
O_2N–C$_6$H$_4$–Me (para)	AcOH	21.0	58.6 ± 1.8	14.94 ± 0.19	[41, 42]
O_2N–C$_6$H$_4$–Me (meta)	AcOH	24.6	57.5	14.57	[41]
NO_2–C$_6$H$_4$–Me (ortho)	AcOH	29.7	51.1	13.44	[43]
O_2N–C$_6$H$_4$–CH$_2$CH$_3$ (para)	AcOH	10.2	53.2	14.79	[38]
O_2N–C$_6$H$_4$–CH$_2$CH$_3$ (meta)	AcOH	13.7	54.1	14.71	[38]
Et_2O	H_2O	49.1	55.3	12.63	[35]
$(ClCH_2CH_2)_2O$	CH_3CN	49.1	61.7	13.47	[26]
Bu_2O	CH_3CN	49.1	49.0	11.71	[26]
$Me_2CHCH(OMe)_2$	$MeC(O)OEt$	30.8	46.6	12.79	[33]
$Me_3CCH(OMe)_2$	$MeC(O)OEt$	30.8	48.6	13.05	[33]
$Me(CH_2)_5CH(OMe)_2$	$MeC(O)OEt$	30.8	46.6	12.80	[33]
$MeOCH_2CH(OMe)_2$	$MeC(O)OEt$	30.8	50.2	13.26	[33]
$MeOCH(OMe)CH_2Cl$	$MeC(O)OEt$	30.8	52.4	13.53	[33]
$MeOCH_2CH_2OMe$	CH_3CN	49.1	55.9	12.70	[26]
tetrahydrofuran-2-carbaldehyde (O, H, H)	CH_3CN	41.2	47.1	12.10	[26]

Table 3. (Contd.)
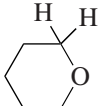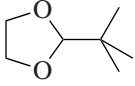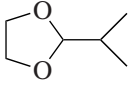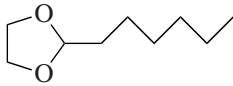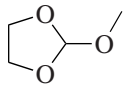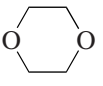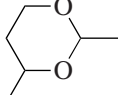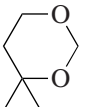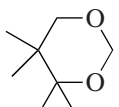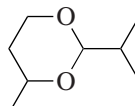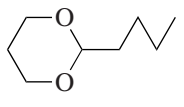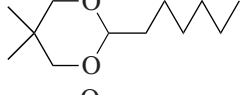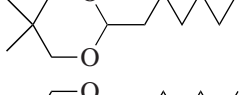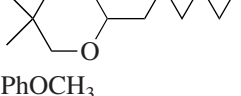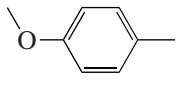
Reactants	Solvent	ΔH, kJ/mol	E, kJ/mol	br_e, $(kJ/mol)^{1/2}$	Reference
(structure)	CH₃CN	51.3	52.6	12.06	[26]
(structure)	MeC(O)OEt	26.6	41.2	12.36	[33]
(structure)	MeC(O)OEt	26.6	41.4	12.39	[33]
(structure)	MeC(O)OEt	26.1	42.6	12.59	[33]
(structure)	MeC(O)OEt	27.6	42.9	12.53	[33]
(structure)	H₂O	55.3	62.4	13.10	[44]
(structure)	H₂O	28.5	51.9	13.61	[44]
(structure)	H₂O	39.4	57.5	13.61	[44]
(structure)	H₂O	38.0	56.4	13.56	[44]
(structure)	H₂O	28.5	52.6	13.70	[44]
(structure)	H₂O	27.6	53.4	13.85	[44]
(structure)	MeC(O)OEt	28.7	42.5 ± 0.43	12.40 ± 0.06	[33]
(structure)	CFCl₃	28.7	42.5	12.39	[33]
(structure)	AcOAc	28.7	42.6	12.40	[33]
PhOCH₃	H₂O	34.6	40.6	11.69	[35]
(structure)	AcOH	12.1	43.4	13.56	[39]
[EtOC(O)]₂CH₂	H₂O	41.3	60.7	13.88	[35]
PhC(O)OCH₃	H₂O	68.0	52.5	10.01	[35]

Table 4. Contribution from the polar interaction ΔE_μ and solvation effect to the activation energy of reactions of O_3 with compounds containing functional groups (the kinetic parameters necessary for the calculation were taken from Tables 2 and 3)
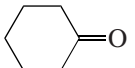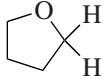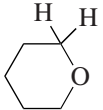
Reactants	Solvent	$br_e,$ $(kJ/mol)^{1/2}$	$\Delta E_\mu + \Delta E_s,$ kJ/mol	$\Delta E_\mu,$ kJ/mol	$\Delta E_s,$ kJ/mol
CH_3OH	H_2O	12.85	−6.2	−6.5	0.3
$MeCH_2OH$	CH_2ClCH_2Cl	12.70	−7.4	−5.8	−1.6
$MeCH_2OH$	AcOH	12.92	−5.7	−5.8	0.1
$MeCH_2OH$	H_2O	12.58	−8.3	−5.8	−2.5
$EtCH_2OH$	H_2O	12.69	−7.5	−7.7	0.2
$PrCH_2OH$	H_2O	12.68	−7.5	−7.2	−0.3
$Me(CH_2)_7OH$	H_2O	12.50	−8.9	−7.2	−1.5
Me_2CHOH	H_2O	12.63	−7.9	−6.2	−1.5
(cyclohexanol)	H_2O	12.80	−6.6	−7.2	−0.6
$MeCH(O)$	H_2O	13.84	1.8	−0.8	2.6
$PhCH(O)$	H_2O	15.11	7.0	2.6	4.4
$MeCH_2C(O)Me$	H_2O	14.52	−6.2	−8.5	2.3
(cyclohexanone)	H_2O	14.38	−7.5	−10.6	3.1
Et_2O	H_2O	12.63	−7.9	−11.1	3.2
$(ClCH_2CH_2)_2O$	CH_3CN	13.47	−1.3	−0.7	−0.6
Bu_2O	CH_3CN	11.71	−14.7	−13.4	−1.3
(tetrahydrofuran)	CH_3CN	12.10	−11.9	−10.4	−1.5
(tetrahydropyran)	CH_3CN	12.06	−12.2	−10.9	−1.3
(dioxolane, tert-Bu)	MeC(O)OEt	12.36	−10.0	−8.2	−1.8
(dioxolane, iPr)	MeC(O)OEt	12.39	−9.7	−7.0	−2.7
(dioxolane, pentyl)	MeC(O)OEt	12.59	−8.2	−2.8	−5.4
(1,4-dioxane)	H_2O	13.10	−4.2	−4.4	0.2
(dimethyl dioxane)	H_2O	13.61	−0.1	−2.8	2.7
(dimethyl dioxane)	H_2O	13.61	−0.1	−1.7	1.6

Table 4. (Contd.)

Reactants	Solvent	br_e, $(kJ/mol)^{1/2}$	$\Delta E_\mu + \Delta E_s$, kJ/mol	ΔE_μ, kJ/mol	ΔE_s, kJ/mol
	H_2O	13.56	−0.5	−1.7	1.2
	H_2O	13.70	0.7	−2.8	3.5
	H_2O	13.85	1.9	−2.8	4.7
	MeC(O)OEt	12.40	−9.7	−9.4	−0.3
	CCl_3F	12.39	−9.7	−9.4	−0.3
	AcOAc	12.40	−9.7	−9.4	−0.3

Reaction	Medium	br_e, $(kJ/mol)^{1/2}$	ΔE_s, kJ/mol	Reference
$HO_2^\cdot + CH_3OH \longrightarrow H_2O_2 + C^\cdot H_2OH$	gas	12.65	0.0	[46]
$HO_2^\cdot + CH_3OH \longrightarrow H_2O_2 + C^\cdot H_2OH$	CH_3OH	12.47	−1.4	[4]
$HO_2^\cdot + CH_3CH(O) \longrightarrow H_2O_2 + CH_3C^\cdot(O)$	gas	12.73	0.0	[47]
$HO_2^\cdot + CH_3CH(O) \longrightarrow H_2O_2 + CH_3C^\cdot(O)$	$CH_3CH(O)$	12.65	−0.6	[4]

It can be seen that for the reactions of the hydroperoxy radical with polar molecules of methanol and acetaldehyde the difference in the solvation of the TS and reactants is insignificant as in the case of the reactions of ozone. The same follows from a comparison of the rate constants of the reactions of the methyl ethyl ketone peroxy radical with this compound [45]. The rate constants of this reaction in different solvents and the ΔE_s values calculated from them are presented below. The calculation was performed by the Arrhenius formula

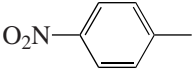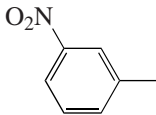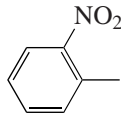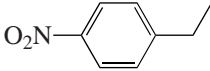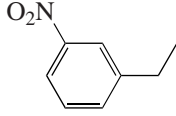$$\Delta E_s = RT\ln(k(\text{Solvent})/k(\text{Decane})). \qquad (19)$$
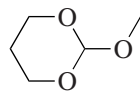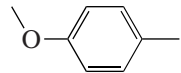
Thus, the analysis of the experimental data for the reactions of ozone with C–H bonds of polar molecules demonstrated a considerable polar effect for most of these reactions. The value of the polar effect is determined by the functional group in the reactant molecule. This allows one to predict the activation energy of the reaction of ozone with any molecule of the studied classes of organic compounds. The polar effect decreases the activation energy of the reaction of ozone with such compounds as alcohols, ethers, ketones, and cyclic acetals by 7–12 kJ/mol. In the reactions with aldehydes, the polar effect exerts virtually no effect on the activation energy.

The polar interaction affects the geometry of the TS: the more strongly the interaction decreases the activation energy, the more strongly the $\varphi(C\ldots H\ldots O)$ angle differs from 180° (see Fig. 1). The $r^{\#}(C\ldots H)$ distance in the TS $(C\ldots H\ldots O)$ elongates with an increase in the enthalpy of the reaction (Fig. 2), in complete accord with the Hammond principle.

The solvation of the TS in a polar solvent, as a rule, reduces the activation energy. However, for most of the studied reactions, the energy of solvation of the TS differs insignificantly from the solvation of the starting reactants. Therefore, the solvation makes a minor contribution to the activation energy. In many cases considered, the effects of the polar interaction and solvation are similar to those for the reactions of peroxy radicals.

Table 5. Total contribution from the polar interaction ΔE_μ and solvation ΔE_s to the activation energy of reactions of O_3 with compounds containing functional groups

Reactants	Solvent	br_e, (kJ/mol)$^{1/2}$	$\Delta E_\mu + \Delta E_s$, kJ/mol
CH_2OHCH_2OH	H_2O	12.96	−5.3
$CH_2OH(CHOH)_4CH(O)$	H_2O	14.32	5.9
$CH_3C(O)OH$	AcOH	11.34	−17.3
$CHCl_3$	H_2O	13.14	−3.9
$CHBr_3$	H_2O	13.58	−0.4
CH_2Cl_2	H_2O	12.62	−8.0
O_2N—(C$_6$H$_4$)—CH$_3$ (para)	AcOH	14.94	5.4
O_2N—(C$_6$H$_4$)—CH$_3$ (meta)	AcOH	14.51	1.6
(C$_6$H$_4$)—CH$_3$ with ortho NO_2	AcOH	13.44	−7.3
O_2N—(C$_6$H$_4$)—CH$_2$CH$_3$ (para)	AcOH	14.79	4.1
O_2N—(C$_6$H$_4$)—CH$_2$CH$_3$ (meta)	AcOH	14.71	3.4
$Me_2CHCH(OMe)_2$	MeC(O)OEt	12.79	−6.6
$Me_3CCH(OMe)_2$	MeC(O)OEt	13.05	−4.6
$Me(CH_2)_5CH(OMe)_2$	MeC(O)OEt	12.80	−6.6
$MeOCH_2CH(OMe)_2$	MeC(O)OEt	13.26	−3.0
$MeOCH(OMe)CH_2Cl$	MeC(O)OEt	13.53	−0.8
$MeOCH_2CH_2OMe$	CH_3CN	12.70	−7.4
2-methoxytetrahydropyran (cyclic acetal)	MeC(O)OEt	12.53	−8.7
$PhOCH_3$	H_2O	11.69	−14.9
MeO—(C$_6$H$_4$)—CH$_3$	AcOH	13.56	−0.5
$[MeCH_2OC(O)]_2CH_2$	H_2O	13.88	2.1
$PhC(O)OCH_3$	H_2O	10.01	−25.9

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