Oxidation of alcohols by dimethyldioxirane

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The kinetics of oxidation of a series of monoatomic alcohols (methanol, 2-propanol, 2-butanol, 2-methyl-1-propanol, 2-chloroethanol, 1,3-dichloro-2-propanol, benzyl alcohol), hydroxyacetic acid, and 1,3-butandiol (ROH) by dimethyldioxirane (**1**) was studied. The reaction kinetics obeys the second order equation $w = k[\mathrm{ROH}][\mathbf{1}]$. The rate constants were measured in the range of 7—50 °C, and the activation parameters were found. To describe the reaction rate constants as a function of the ROH structure, the two-parametric Taft equation was used, which takes into account both the polar and resonance substituent effects. Alcohol oxidation produces the corresponding carbonyl compounds, *viz.*, ketones from secondary alcohols and aldehydes from primary alcohols, in yields of at least 80%. The results were explained by the competition of the molecular (oxenoid) and radical mechanisms. The introduction of electron-withdrawing substituents into the alcohol molecule increases the contribution of the radical channel of the reaction.

Key words: dimethyldioxirane, alcohols, rate constants, free radicals.

In recent years, dioxiranes have been widely used for the oxidative functionalization of organic compounds. They possess some advantages as compared to conventional oxidants: mild conditions and high rates of reactions; chemo-, stereo-, and regioselectivity; simple procedures of oxidation and separation of the reaction products. The reactions between alcohols and dioxiranes have been studied previously.[1—6] The reaction between secondary alcohols (*viz.*, propane-2-ol, octane-3-ol, cyclobutanol, cyclohexanol, norborneol, and α-methylbenzyl alcohol) and methyl(trifluoromethyl)dioxirane affords the corresponding ketones. The oxidation of butan-1-ol by methyl(trifluoromethyl)dioxiranes produces butyric acid, whereas a tertiary alcohol, 2-methylpropan-2-ol, does not react with dioxiranes.[1] The acetophenone derivatives are the main products of the reaction of dimethyldioxirane with *p*-substituted α-methylbenzyl alcohols.[2] Linear and cyclic 1,2- and 1,3-diols are oxidized by dimethyldioxirane and methyl(trifluoromethyl)dioxirane to α- and β-hydroxyketones.[3—6]

The kinetics of the oxidation of cyclohexanol by methyl(trifluoromethyl)dioxirane[1] and that of *p*-substituted α-methylbenzyl alcohols by dimethyldioxiranes[2] have been studied. However, the activation parameters have been measured in only a narrow (20 °C) temperature range.

This work is aimed at the study of the products, kinetics, and mechanism of the interaction between dimethyldioxirane and aliphatic monoatomic alcohols: methanol (**2**), propan-2-ol (**3**), butan-2-ol (**4**), 2-methylpropan-1-ol (**5**), 2-chloroethanol (**6**), and 1,3-dichloropropan-2-ol (**7**), as well as the related compounds: hydroxyacetic acid (**8**), benzyl alcohol (**9**), and butane-1,3-diol (**10**) (ROH) in an acetone solution at 7.0—50.0 °C.

Experimental

Acetone of high purity grade was purified by distillation. Dimethyldioxirane (**1**) was synthesized by a known procedure[7]; water was removed from an acetone solution of dioxirane by freezing. Notably, drying the solution of **1** with magnesium sulfate is preferred, as was proposed,[8] accelerates the thermal decomposition of dioxirane.

Dimethyldioxirane was identified and analyzed as has been reported previously.[7]

Alcohols **2**—**7** were distilled after preliminary drying. Hydroxyacetic acid was recrystallized from water; benzyl alcohol and butane-1,3-diol were purified according to known procedures.[9]

The reaction kinetics were studied by dioxirane consumption. A change in the concentration of **1** during the reaction was monitored spectrophotometrically at λ_{max} = 335 nm (ε = 10 L mol^{-1} cm^{-1}) on a Specord M-40 instrument. A solution of ROH in acetone was placed in a quartz cuvette, which was maintained at 7—50 °C in a cuvette chamber of the spectrophotometer. A specified amount of the **1** solution in acetone was added. The cuvette was purged, when it was necessary, by oxygen (1.5 min) or argon, and variation in the absorbance of **1** was monitored. The starting concentrations of **1** and **2**—**10** were varied in the ranges of $(0.7-4.4)\cdot10^{-2}$ mol L^{-1} and $(3.9-30)\cdot10^{-1}$ mol L^{-1}, respectively. Acetone or the $Me_2CO-CCl_4$ and $Me_2CO-MeCN$ mixtures were used as the solvents.

The oxidation products were analyzed by ^{1}H and ^{13}C NMR spectroscopies on a Bruker AM-300 instrument (300 and 75 MHz, respectively); Me_4Si was used as the standard and acetone-d_6 and tetrachloromethane as the solvents. To estimate quantitatively the yields of the products, benzene or *tert*-butanol were used as the internal standards. Additionally, the reaction

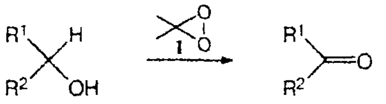
Published in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1338—1343, August, 2000.

products were analyzed by GLC on a Chrom-5 instrument (3.5 m×3 mm column; immobile phase SE-30).

Results and Discussion

Reaction products. When **1** reacts with the secondary alcohols **3**, **4**, **7**, and **10**, the corresponding ketones form in high yields. The primary alcohols **2**, **5**, **6**, and **8** are oxidized to aldehydes (Table 1). The yields of the reaction products based on consumed **1** ($\Delta[R^1R^2CO]/\Delta[\mathbf{1}]$) are high (80—99%).

Scheme 1



2—10

	R¹	R²		R¹	R²
2	H	H	**7**	CH_2Cl	CH_2Cl
3	Me	Me	**8**	H	C(O)OH
4	Me	Et	**9**	H	Ph
5	H	Pr^i	**10**	Me	C_2H_4OH
6	H	CH_2Cl			

The effect of O_2 on the composition and yield of the reaction products was found for compounds **6**—**8** (see Table 1). In the absence of oxygen, the conversion of the substrates is low. The conversion of ROH and, hence, the yields of the oxidation products increase in the presence of O_2 as compared to those in deaerated solutions, and acids also form in this case. A low conversion of ROH in an inert atmosphere is due to the radical-chain decomposition of dioxirane. As is well known,[10] solutions of dioxirane are more stable in the presence of O_2 than in an inert atmosphere.

Table 1. The products of oxidation of alcohols **2**—**10** by dimethyldioxirane (25 °C, acetone is the solvent)

Alcohol	Product	Yield (%)[a]
2	Paraform	90
3	Acetone	95
4	Butan-2-one	96
5	2-Methylpropanal	95
6[b]	2-Chloroethanal	90
	Cloroacetic acid	7
6[c]	2-Chloroethanal	5
	Chloroacetic acid	—
7[b]	1,3-Dichloropropanone	80
7[c]	1,3-Dichloropropanone	10
8[b]	Glyoxalic acid	79
	Oxalic acid	10
8[c]	Glyoxalic acid	6
9	Benzaldehyde	99
10	1-Hydroxy-3-butanone	92

[a] The yield of the products based on dioxirane consumed.
[b] In O_2 atmosphere.
[c] Purging with argon.

Table 2. Temperature dependence of the rate constant k and the activation parameters of the reactions of alcohols **2**—**10** with dimethyldioxirane (acetone is the solvent)

Alcohol	T /°C	$k \cdot 10^4$ [a]	E_a	$\Delta H^{\neq}_{297}$	$\Delta G^{\neq}_{297}$	log$A$	$\Delta S^{\neq}_{297}$ [b]
			kcal mol^{-1}				
2	24.5	2.4	16.1	15.5	22.4	8.2	−23.0
	32.0	3.5					
	39.5	9.3					
3	12.0	49.0	17.0	16.6	19.8	10.9	−10.8
	19.4	116.3					
	25.0	185.4					
	30	224.8					
	34.5	406.3					
	39.7	819.2					
4	7.0	67.6	9.32	8.7	19.8	5.1	−37.2
	14.7	107.0					
	24.5	159.0					
	32.0	283.7					
5	7.0	20.5	11.7	11.1	20.3	6.5	−31.0
	14.1	34.5					
	24.5	31.8					
6[c]	24.5	1.0	17.6	17.0	22.9	9.0	−19.6
	31.0	1.9					
	40.0	3.3					
	49.5	1.1					
7[c]	25.2	0.49	10.3	9.7	23.0	3.2	−44.9
	32.0	0.68					
8[c]	24.5	1.3	18.0	17.4	23.1	9.1	−18.9
	32.0	0.9					
	40.0	1.6					
	50.0	1.4					
9	19.4	33.1	5.8	5.2	20.7	1.9	−52.0
	24.5	33.4					
	30.0	47.0					
10	27.0	177±4	—	—	—	—	—

[a] L mol^{-1} s^{-1}.
[b] Cal mol^{-1} K^{-1}.
[c] The kinetic data were obtained from the initial segments of the kinetic curves (see Fig. 3).

The oxidation of **10** is very regioselective: 1-hydroxybutan-3-one forms with a high yield (see Table 1). This fact is in line with the kinetic data, which show that secondary alcohols are oxidized faster than primary alcohols (Table 2).

The reaction kinetics. The reaction kinetics were studied at $[\mathbf{1}]_0 << [ROH]_0$, where $[\mathbf{1}]_0$ and $[ROH]_0$ are the starting concentrations of dimethyldioxirane and a substrate, respectively (the thermal decomposition of **1** can be neglected in these conditions). The kinetic curves for compounds **2**—**5**, **9**, and **10** are described by a first-order equation with a high correlation coefficient (0.98—0.999) (Fig. 1). The first-order effective rate constants $k_{eff} = =k \cdot [ROH]^n$ (k is the second-order rate constant) were calculated from the anamorphoses of the kinetic curves. The rate constant k_{eff} is independent of the content of O_2 in the reaction mixture and the con-

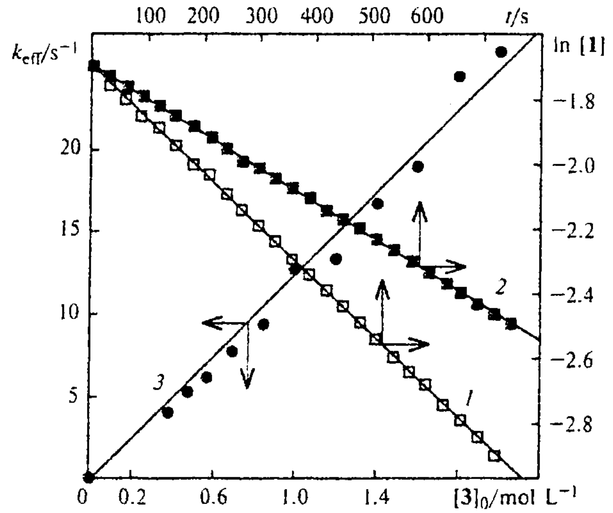


Fig. 1. Semi-logarithmic anamorphoses of the kinetic curves of **1** consumption in the presence of **3** at $[3]_0$ = 0.39 (*1*) and 0.57 mol L^{-1} (*2*) at 25.0 °C and the effective rate constants of **1** consumption as a function of concentration of **3** (*3*).

centration of **1**. The linear dependence of k_{eff} on $[ROH]_0$ indicates the first order with respect to ROH (see Fig. 1). Hence, the kinetic equation for the reaction is

$$-d[\mathbf{1}]/dt = k[\mathbf{1}]\cdot[ROH].$$

The temperature dependence of the rate constants for all the ROH studied was measured, and the activation parameters were found (see Table 2). As can be seen, an increase in the activation energy is accompanied by an increase in the preexponential factor (a compensation effect) (Fig. 2).

$$E_a = (3.2\pm1.6) + (1.5\pm0.6)\lg A \quad (r = 0.933),$$

$$\Delta H^{\neq} = (21.9\pm3.7) + (0.32\pm0.12)\cdot\Delta S^{\neq}.$$

The above dependence is also valid for the reported data[2] on *p*-methoxy-α-methylbenzyl alcohol (**11**), α-methylbenzyl alcohol (**12**), *p*-fluoro- (**13**), *p*-chloro- (**14**), *p*-bromo- (**15**), and *p*-methyl-α-methylbenzyl alcohol (**16**) (see Fig. 2). The compensation effect likely points to the same reaction mechanism for all the substrates.

The kinetic curves of the dioxirane consumption for compounds **6**—**8** are S-shaped (Fig. 3). The O_2 content in the reaction mixture affects substantially the thermal decomposition of dimethyldioxirane.[10] This fact was attributed to inhibition of the alkyl radicals-induced decomposition of dimethyldioxirane. Oxygen is chemically bound with increasing conversion of **1**, and at the deep stages, the process is significantly accelerated. The preliminary purging of the starting ROH solution with argon decreases the induction period (see Fig. 3). A sharp increase in the reaction rate after the removal of O_2 from the solution points to a change in the mechanism. The amount of consumed inhibitor (O_2) allows for estimation of the efficiency of the escape of free radicals during the process. The stoichiometry of the reaction is the following: the interaction between one molecule of **1** and ROH produces two carbon-centered radicals in a sequence of fast reactions. The radicals add two molecules of O_2 and undergo recombination; as a result, one O_2 molecule is recovered in the solution. At higher O_2 conversions, it cannot trap all alkyl radicals; meanwhile, the chains are terminated by the cross reaction

$$R^{\cdot} + ROO^{\cdot} \rightarrow ROOR$$

without dioxygen evolution. Thus, during all the induction period, the equimolar stoichiometry of **1** con-

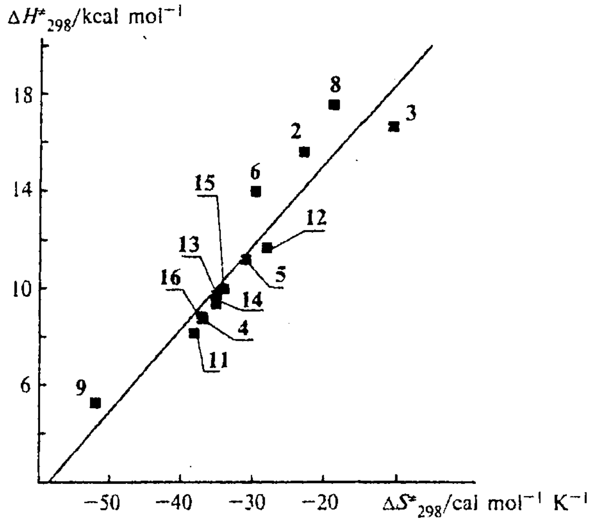


Fig. 2. Dependence of $\Delta H^{\neq}$ on $\Delta S^{\neq}$ for a series of compounds.

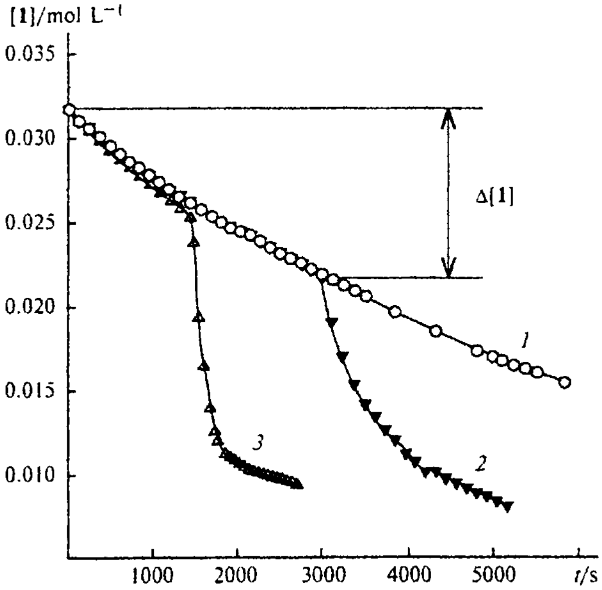


Fig. 3. The kinetic curves for **1** consumption in the presence of **8** (24.5 °C, $[8]_0$ = 1.98 mol L^{-1}): continuous purging with dioxygen (*1*); purging with dioxygen before a run for ~2 min (*2*); the solution was purged with argon (*3*).

sumption in the radical channel of the reaction is maintained. Hence, the $[O_2]_0/\Delta[\mathbf{1}]$ ratio (where $\Delta[\mathbf{1}]$ is the amount of **1** decomposed during the induction period) characterizes the escape of free radicals during the reaction.

It is seen in Fig. 3 that $9.25 \cdot 10^{-3}$ mol L^{-1} of dioxirane **1** is consumed during the induction period of the oxidation of hydroxyacetic acid at 25 °C. The concentration of O_2 in the acetone solution at this temperature is $1.83 \cdot 10^{-3}$ mol L^{-1}. The solubility of O_2 in the reaction mixture was taken to be equal to its solubility in acetone.[11] Thus, the yield of the radicals is $\xi = [O_2]_0/\Delta[\mathbf{1}] = 0.20$. For compounds **6** and **7**, ξ is 0.13 and 0.20, respectively (ξ was calculated at the concentration of ROH equal to 9 vol. %). A significant increase in the escape of the radicals into the bulk was observed for the alcohols containing the electron-withdrawing groups. This is likely due to the fact that these substituents stabilize to a lesser extent the positive charge on the reaction center in the transition state.[12,13]

Medium effect. Alcohols tend to self-association, and this can essentially affect their reactivity.[14,15] The dependence of k_{eff} on [ROH] for **3** is linear in a wide concentration range (0.39—2.0 mol L^{-1}). This indicates that the effect of association of the alcohol molecules on the reaction is absent.

The effect of the solvent polarity on the rate of consumption of **1** was studied in the $Me_2CO-CCl_4$ and $Me_2CO-MeCN$ mixtures. Replacement of the nonpolar solvent CCl_4 ($\varepsilon = 3.4$) by polar acetonitrile ($\varepsilon = 36.6$) does not change the rate constants (Table 3), indicating a small polarity of the transition state.

The effect of the ROH structure on the rate constant of the reaction. As seen in Table 2, the reactivities of ROH at 25 °C change in the following sequence: 1,3-dihydroxypropan-2-ol < hydroxyacetic acid ≤ 2-chloroethanol < methanol < 2-methylpropan-1-ol ≤ benzyl alcohol < butan-2-ol ≤ butan-1,3-diol ≤ propan-2-ol.

Examination of the above results with the Taft one-parameter equation[12]

$$\log(k/k_0) = \rho^*\sigma^*$$

does not show a satisfactory correlation ($r < 0.6$) (a fragment >C(OH)H is chosen as the reaction center, and k_0 is the rate constant for **2**). This is likely due to the fact that it is insufficient to take into account only the inductive effect on the rate constant. Therefore, our findings were examined with the modified two-parameter Taft equation, which takes into account both polar and resonance effects of substituents[16]

$$\log(k/k_0) = \rho^*\sigma^* + r^*\sigma^r$$

or

$$(1/\sigma^*)\log(k/k_0) = \rho^* + r^*\sigma^r/\sigma^*.$$

Here σ^*, σ^r are the polar and resonance constants of substituents, respectively, r^* is the proportionality coefficient, and k_0 is the rate constant for the reaction of **1** with methanol. Compound **9** was removed from the correlation (Fig. 4). The following values of σ^r (σ^*) were used for the correlation: **3**, 0.8 (−0.19); **4**, 0.70 (−0.21); **5**, 0.534 (−0.125); **6**, 0.28 (0.385); **7**, 0.56 (0.77); **8**, 0.40 (1.05); and **10**, 1.8 (1.454). According to Fig. 4, $\rho^* = -1.7\pm0.1$ ($r = 0.988$). The ρ^* value calculated by the Taft equation with allowance for the reported data[17] and the steric effect[18] is −0.77 ($\rho^s = 4.4$).

The negative ρ^* value indicates that the positive charge of the reaction center increases in the transition state and the introduction of electron-donor substituents accelerates the reaction. The ρ^* value is comparatively small and virtually independent of temperature (Table 4). This can indicate that the charge formed in the transi-

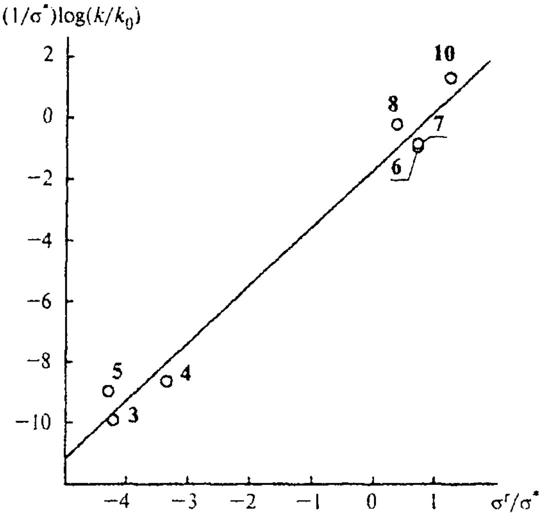


Fig. 4. Dependence of $(1/\sigma^*)\log(k/k_0)$ on σ^r/σ^* at 25 °C, acetone is the solvent.

Table 3. The solvent effect on the oxidation rate for propan-2-ol ($[\mathbf{3}]_0 = 0.44$ mol L^{-1}; $[\mathbf{1}]_0 = 0.04$ mol L^{-1}; 25.0 °C)

Solvent	Molar ratio of the components of the solvent	$\varepsilon_{\mathrm{mix}}$*	$k_{\mathrm{eff}} \cdot 10^{-3}$ /s^{-1}
$Me_2CO-CCl_4$	0.5 : 3.5	3.4	5.4±0.1
	4 : 0.7	17.3	4.95±0.08
$Me_2CO-MeCN$	4.6 : 0.6	22.9	4.69±0.05
	0.5 : 6.4	36.6	5.1±0.1

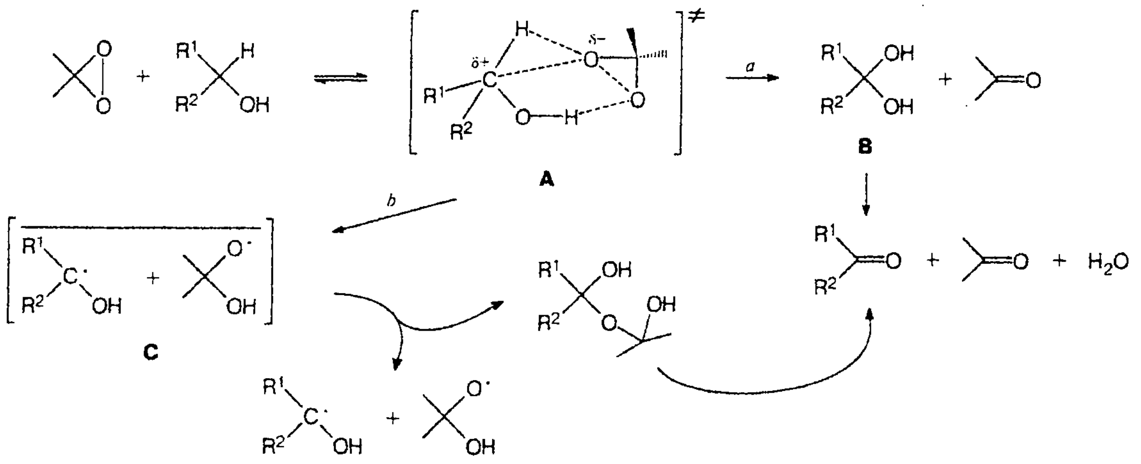
* See Ref. 23.

Table 4. Temperature dependence of ρ^* and r^*

T/°C	r^*	ρ^*	r
10.0	2.4±0.7	−1.9±0.5	0.986
24.5	1.9±0.3	−1.7±0.1	0.988
30.0	2.2±0.4	−1.6±0.3	0.995
40.0	2.1±0.4	−1.7±0.3	0.994

Note. Acetone is the solvent; r is the correlation coefficient.

Scheme 2



tion state is not high and is stabilized mainly by the O atom of the OH group rather than the substituent.[13] A slight effect of the solvent polarity on the reaction rate constant (see Table 3) also confirms a low-polarity nature of the transition state.

Reaction mechanism. The above experimental data can be rationalized in the context of the competition between the molecular ("oxenoid") and radical mechanisms (Scheme 2).

On the basis of the previously reported data,[19,20] one can suggest that the transition state of the **A** type (see Scheme 2) results in either the intermediate **B**, which rapidly transforms to the carbonyl compound, or to the radical pair **C**.

The following facts give evidence in favor of the molecular pathway *a*:

— high yields of carbonyl compounds, ketones, and aldehydes (see Table 1), can be easily explained by the formation of the tetrahedral intermediate **B**;

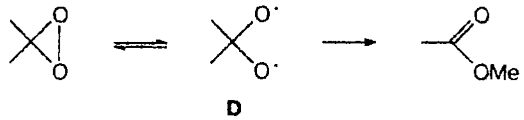
— the formal-kinetic features of the reaction (the first order with respect to dioxirane and ROH);

— a low value of the entropy of activation, $\Delta S^{\neq} = -10.8$ to -52 cal mol^{-1} K^{-1} (see Table 2), points to a highly ordered transition state of the **A** type.

However, the effect of O_2 on the reaction rate and the dependence of the yield of the oxidation products on the O_2 concentration (see Table 1) are at variance with the molecular mechanism (oxidation of compounds **6**—**8**, see Fig. 3). The effect of oxygen is associated with the competing reaction pathway *b*. The radical pair **C** forms in the singlet state and, as a result, the probability of intracell recombination is high. Therefore, one can expect a low escape of the radicals into the bulk. This is the reason why the fraction of radicals "trapped" by dioxygen is small and the yields of carbonyl compounds are high (see Table 1). A comparatively low ρ^* value (see Table 4) also does not contradict the radical mechanism.[21]

In conclusion note that along with the radical mechanism (a substrate-induced homolysis), an alternative radical process, the molecular homolysis of the O—O bond, producing the bis-oxyisopropyl biradical **D**, is discussed in the literature (Scheme 3).

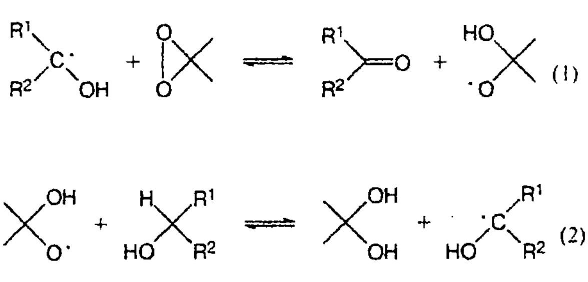
Scheme 3



However, biradical **D** isomerizes into methyl acetate with a low activation energy.[22] Hence, H atom abstraction from the ROH molecule is improbable.

Another possibility is the oxidation of alcohols to ketones through a radical-chain mechanism (Scheme 4), which is similar to the known mechanism of alcohol oxidation by diacylperoxides.[24]

Scheme 4



When the chains are assumed to be generated by the interaction between dioxirane and alcohol and the chain termination occurs through the reaction of $Me_2C(O^\cdot)OH$ with hydroxyalkyl radical, the reaction kinetics should be first-order with respect to both dioxirane and alcohol.

Our experimental data disagree with this mechanism. The $\Delta[R^1R^2CO]/\Delta[\mathbf{1}]$ value for alcohols **2**—**5**, **9**, and **10** is the same both in the presence and absence of O_2. In an O_2 atmosphere, the hydroxyalkyl $R^1R^2C^{\cdot}(OH)$ radicals rapidly transform into peroxyl radicals, which are inactive in the reaction with **1**.[25] Hence, the accumulation of R^1R^2CO through reaction (1) in Scheme 4 can be neglected.

As shown above, free-radical processes play an important role in the interaction between dioxirane and alcohols **6**—**8** in an inert atmosphere (ξ = 0.13—0.20). In this case, the alkyl radical-induced decomposition of **1** occurs,[25] which manifests itself in the S-like character of the kinetic curves of **1** consumption (see Fig. 3). Nevertheless, the yields of carbonyl compounds due to the oxidation of **6**—**8** in an inert atmosphere become lower by an order of magnitude, indicating the low probability of reactions (1) and (2) in Scheme 4.

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Received September 6, 1999;
in revised form February 23, 2000