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Products, kinetic regularities, and mechanism of thermal decomposition of ethyl(methyl)dioxirane

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The products and kinetic regularities of thermal decomposition of ethyl(methyl)dioxirane (EMD) were studied. The consumption of EMD occurs *via* four parallel pathways: two isomerizations to ethyl acetate and methyl propionate, solvent oxidation *via* insertion of the oxygen atom into the C—H bond of a solvent molecule (butanone), and hydrogen atom abstraction from the solvent by dioxirane with radical escape from the cage. The contribution of the latter route to the oxidation of butan-2-one at 35 °C is 43%. Alkyl radicals initiate EMD decomposition in an inert atmosphere. The activation parameters of EMD isomerization to esters and the reaction of EMD with butanone were determined. The isomerization of EMD was studied by the DFT method. The geometric parameters were optimized at the UB3LYP level using the 6-31G** and/or 6-311+G** basis sets. The calculated energies were corrected taking into account zero-point vibrations. The theoretical results are in good agreement with experimental data. The mechanism of EMD thermolysis is considered.

Key words: dioxiranes, quantum chemical calculations, reaction rate constants, free radicals, peroxides.

Strained cyclic peroxides, *viz.*, dioxiranes, find wide use in organic chemistry for the oxidation of compounds of different classes.[1,2] Dioxiranes can efficiently be used only taking into account their stability and mechanisms of transformations.

A series of dioxiranes has been synthesized to the present time.[3] However, there are only few works devoted to studies of kinetic regularities and decomposition products of different dioxiranes.

We have previously[4] studied in detail the kinetic regularities and decomposition products of dimethyldioxirane in acetone and CCl_4. At temperatures lower than +10 °C the major thermolysis product is methyl acetate. At higher temperatures the decomposition in acetone in the presence of oxygen proceeds *via* three parallel pathways: isomerization to form methyl acetate, insertion of the O atom into the C—H bond of a solvent molecule (acetone), and proton abstraction from the solvent by dioxirane to form a radical pair. The contribution of the latter pathway at 56 °C is 23%. "Blank" consumption of dimethyldioxirane induced by alkyl radicals is observed in an inert atmosphere.

Several works on the decomposition of several other dioxiranes as well were published.

It has been shown[5] by mass spectrometry that in the gas phase at the temperatures from –120 to –50 °C the decomposition of dioxirane (H_2CO_2) affords CO, CO_2, H_2O, H_2, and $H^•$. These data have been confirmed.[6] A proposed mechanism assumes the O—O bond cleavage followed by the isomerization of the bis(oxy)methylene biradical that formed to formic acid with its further decomposition.

The products of thermal decomposition of methyl(trifluoromethyl)dioxirane in different solvents are methyl trifluoroacetate, trifluoromethyl acetate, methyl acetate, and CO_2. The mechanism of the process includes the formation of the biradical with its further decomposition to CO_2 and radicals $^•CH_3$ and $^•CF_3$ that induce the chain-radical decomposition of dioxirane.[7] The presence of oxygen in the system decreases sharply the yield of esters and retards thermolysis.

Dimesityldioxirane isomerizes to form ester in both solutions ($CFCl_3$, butan-2-one) and crystals.[8,9] The decomposition of cyclohexanonedioxirane at –25 °C in cyclohexanone affords oxepan-2-one.[10]

Thus, the homolysis of the O—O bond of the three-membered ring to form an unstable radical, whose decomposition depends on substituents, is common for the thermal decomposition of dioxiranes. The thermolysis process is also affected by the solvent and temperature.

In the present work, we studied the thermal stability of ethyl(methyl)dioxirane (EMD) in a solution of butanone

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and its mixtures with CCl_4. The composition of the products was determined and the kinetic regularities of EMD decomposition were studied. Quantum chemical modeling of selected steps of the process was performed using the density functional theory (DFT).

Experimental

Butan-2-one (**1**) was dried over molecular sieves A4 and distilled in argon prior to use. Tetrachloromethane (reagent grade) was purified using a standard procedure.[11] Ethyl(methyl)dioxirane was synthesized by an earlier described method.[12] The dioxirane concentration was determined by the iodometric and/or spectrophotometric method. Dioxirane solutions were dried by freezing out water from the solutions at –40 °C. The molar absorption coefficient (ε) of EMD was determined from the data of iodometric titration and measurements of the absorbance of the solution at the wavelength 335 nm; ε_{335}(EMD) = 18.0 L mol^{-1} cm^{-1} in methyl ethyl ketone. The kinetic regularities of EMD consumption were studied on a Specord M-40 instrument (Carl Zeiss Jena) in a quartz cell (l = 0.5 cm) from a decrease in the absorbance at the wavelength λ = 335 nm in the temperature interval 20—70 °C. The initial dioxirane concentration was varied within 0.01—0.13 mol L^{-1}. Before the reaction a dioxirane solution was purged with oxygen or argon. The products were analyzed chromatographically (Shimadzu GC-9A, capillary column OV101, l = 30 m, internal standard *n*-decane) and by gas chromatography coupled with mass spectrometry (GC-MS) (HP 5890 Series II instrument, HP5 capillary column, l = 30 m, HP5972 mass-selective detector). NMR spectra were recorded on a Bruker AM-300 spectrometer (standard Me_4Si, solvent $CDCl_3$).

Methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, butanedione, and acetaldehyde were identified by comparison of the retention times and mass spectra with the data for reference spectra.

3-Hydroxybutan-2-one. Mass spectrum (EI, 70 eV), m/z (I_{rel} (%)): 88 [M]$^+$ (15), 73 [M – Me]$^+$ (5), 59 (1), 57 (1), 45 (100), 43 (88). The obtained spectrum is well consistent with the previously described spectra.[13,14] The low intensity of the peak of the fragmentation ion with m/z = 57 indicates that the signal from 1-hydroxybutan-2-one,[15,16] which is one of possible products, is absent in this chromatographic peak.

1-Methyl-2-oxopropyl acetate and 3-(1-oxopropoxy)butan-2-one. After dioxirane was completely consumed at 50 °C in a deoxygenated solution of butanone, a sample was taken for chromatographic and GC-MS analyses. The solvent was evaporated, and the residue was divided using preparative GLC (SE-30, l = 2 m, d = 12 mm). ^{1}H and ^{13}C NMR spectra were recorded for the obtained fractions of heavy products. According to the spectral data, the major product is 1-methyl-2-oxopropyl acetate and the second one is 3-(1-oxopropoxy)butan-2-one. The recorded ^{1}H, ^{13}C NMR and mass spectra are well consistent with published data.[17]

3-Hydroperoxybutan-2-one. After the complete consumption of EMD during thermolysis, peroxide was found in oxygen-saturated butanone solutions by iodometric titration under the conditions of determination[18] of peroxy acids, hydrotrioxides, and diacyl peroxides. It can be asserted that the peroxide formed is not peroxy acid, because after the peroxide that formed was reduced with dimethyl sulfide followed by the treatment of the solution with CH_2N_2 the surface areas of the peaks of esters remained unchanged and no new peaks appeared. Arsenometric titration[18] using Et_3As showed the absence of diacyl peroxides. Thus, the found peroxide is hydroperoxide. Unfortunately, it is very difficult to detect this product by spectral methods. However, since the reduction of hydroperoxides with triphenylphosphine affords the corresponding alcohols[18] and only one product containing the hydroxyl group (3-hydroxybutan-2-one) was found in the products, after the complete hydroperoxide consumption in the reaction with phosphine in our case, we can assume that the peroxide observed in the system is 3-hydroperoxybutan-2-one.

Determination of oxygen solubility. The oxygen concentration in a solution of compound **1** was determined using a known procedure.[19] The obtained data are presented below.

T/°C	20.0[20]	25.2	30.0	35.2	40.4
$[O_2]\cdot10^3$/mol L^{-1}	10.8	10.7	10.3	9.70	9.19
T/°C	44.8	50.5	54.8	65.0	71.0
$[O_2]\cdot10^3$/mol L^{-1}	8.65	8.29	7.94	6.35	4.90

Procedure of quantum chemical calculations. Density functional (DFT) calculations were performed by the Becke three-parameter hybrid exchange functional (B3)[21,22] with the Lee—Yang—Parr correlation functional (LYP)[23] (hereinafter B3LYP). The standard[24] two- and three-exponential basis sets 6-31G(d,p) and 6-311+G(d,p) were used. All geometric parameters for molecules, intermediates, and transition states were optimized without symmetry restraints. The nature of the optimized structures was determined by analysis of the eigenvalues of the Hesse matrix, which is a matrix of the second energy derivatives with respect to coordinates calculated geometrically. The calculated energies were corrected taking into account zero-point vibrational energies (ZPE) for the corresponding structures taken without a correction coefficient.

All quantum chemical calculations were performed using the GAUSSIAN-98 program package.[25]

Results and Discussion

Products of EMD decomposition. The composition of the EMD thermolysis products depends on the temperature and oxygen concentration in solution. The results of analysis of the solutions after complete dioxirane consumption are presented in Table 1.

The study of the thermal decomposition products in oxygen-saturated solutions showed that the non-radical transformation of EMD into esters and the interaction of dioxirane with compound **1** were parallel. At 10 °C the rate of dioxirane isomerization to esters prevails over the reaction of solvent oxidation, and the temperature increase results in the involvement of the solvent in thermal decomposition (the appearance of hydroxybutan-2-one in the products). Compound **1** can be oxidized *via* both the mechanism of oxygen atom insertion (without participation of radicals) and involving free radicals, as has been earlier found for dimethyldioxirane.[4] The latter reaction pathway can result in the initiated oxidation of

Table 1. Products of the EMD thermolysis in butan-2-one

Atmosphere	T/°C	Product	Yield* (%)
O_2	10	Ethyl acetate	85
		Methyl propionate	11
	50	Ethyl acetate	58
		Methyl propionate	7
		3-Hydroxybutan-2-one	49
		Butanedione	8
		Acetaldehyde	1
N_2	50	Ethyl acetate	30
		Methyl propionate	2
		Methyl acetate	4
		Ethyl propionate	8
		3-Acetoxybutan-2-one	41
		3-Propoxybutan-2-one	11

* The yield based on consumed dioxirane is presented.

the solvent with oxygen.[26] After EMD decomposition, 3-hydroperoxybutan-2-one was found in oxygen-saturated solutions of compound **1** along with the products presented in Table 1. The decomposition of EMD with an initial concentration of 0.06 mol L^{-1} at 30 °C results in the formation of 0.03 M hydroperoxide. This is an incontestable fact that this system involves the initiation reaction being faster than the reaction of compound **1** with oxygen, which is insufficient[26] at this temperature for the appearance of the indicated amount of the products. In our opinion, this reaction can be the interaction of EMD with the solvent.

Kinetics of EMD thermolysis in an oxygen atmosphere. The thermal decomposition of EMD in oxygen-saturated solutions of compound **1** occurs with low rates. For example, at 30 °C the conversion is 13% for 10^4 s. The kinetic curves are linearized with a high correlation coefficient in the coordinates of a first-order equation. The apparent rate constant of EMD thermolysis (k_{app}) is independent of the EMD concentration. The kinetic order with respect to dioxirane is first.

Purging of a dioxirane solution with an inert gas for 1 min decreases the oxygen concentration, which results in the shortening of the induction period (Fig. 1). However, before the break in the kinetic curve, the reaction rate remains the same as in experiments where the presence of oxygen was maintained during the whole kinetic experiment. Unfortunately, at temperatures above 40 °C in the presence of oxygen, no well reproducible kinetic data can be obtained at a high conversion of dioxirane (the kinetic curves have a variable order) and, therefore, the apparent rate constants were calculated from the initial regions of the kinetic curves. This is related, most likely, to the consumption of the accumulated hydroperoxide and its involvement in the process. The radicals formed upon hydroperoxide decomposition, possibly, begin to attack dioxirane, resulting in the deviation of the order with respect to EMD from the first one. The reactions of EMD with the thermolysis products, such as acetaldehyde, which is oxidized, according to our data, with the rate constant 10^{-1}—10^{-2} L mol^{-1} s^{-1}, also occur. To confirm an assumption on the possibility of violation of the kinetic data due to the decomposition of the accumulated hydroperoxide, we studied its stability. At 60 °C in the presence of oxygen, the concentration of hydroperoxide ($[MeC(O)CH(OOH)Me]_0$ = 0.03 mol L^{-1}) decreases by 28% for 2 h, whereas in an inert atmosphere this decrease is 58%. At 30 °C the hydroperoxide concentration for the same time period remains virtually unchanged. Therefore, hydroperoxide decomposition can make a substantial contribution to the overall pattern of the process at temperatures higher than 30 °C.

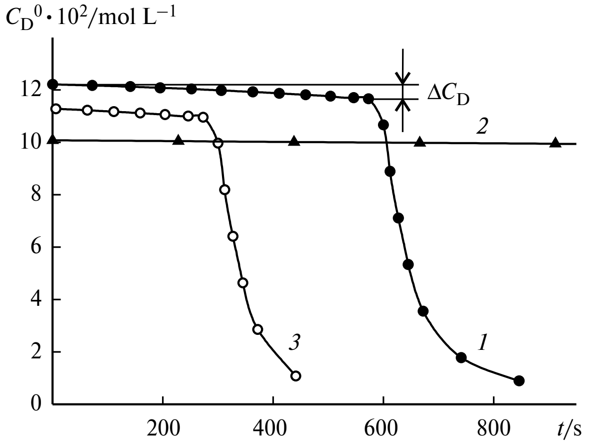


Fig. 1. Kinetic curves of the ethyl(methyl)dioxirane thermolysis at 59 °C in a butan-2-one solution: *1*, single purging of the solution with oxygen for 2 min; *2*, continuous purging with oxygen; and *3*, purging with an inert gas for 1 min; C_D is the EMD concentration.

The temperature effect on k_{app} was studied in a range of 20—60 °C. The overall activation parameters of EMD decomposition (butan-2-one as solvent) were calculated from this dependence

$$\log k_{app} = (7.7\pm0.5) - (73\pm3)/\theta \ (r = 0.996);$$
$$\theta = 2.303RT, \text{ kJ mol}^{-1}.$$

The data on the composition of the decomposition products indicate that the reaction of EMD with compound **1** does occur. To study the contribution of this reaction to the thermal decomposition of EMD, we studied its thermolysis in **1**—CCl_4 mixtures. A decrease in the concentration of compound **1** results in a regular decrease in k_{app} (Fig. 2). This agrees with the conclusion about the competition of mono- and bimolecular channels of EMD consumption made on the basis of analysis of the products. A similar dependence have been observed previously[4] for dimethyldioxirane decomposition in CCl_4—acetone mixtures.

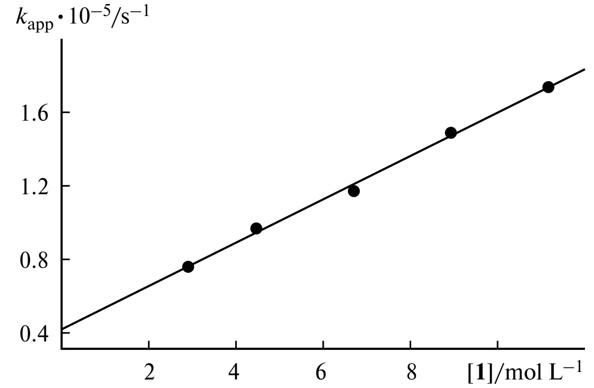
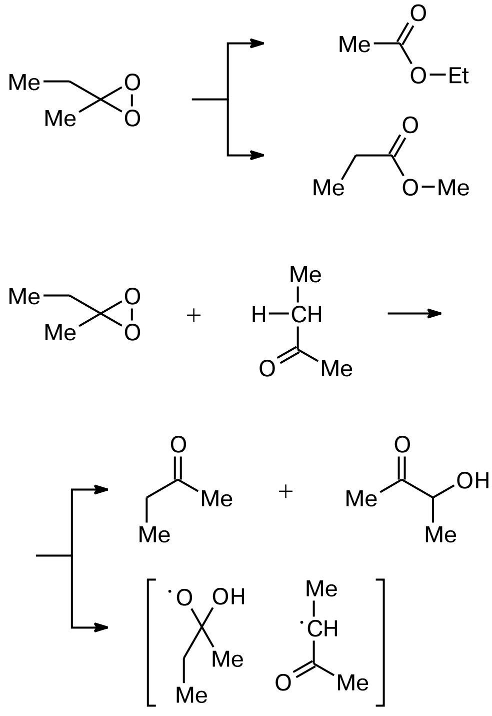


Fig. 2. Plot of the apparent rate constant of the ethyl(methyl)dioxirane thermolysis at 35 °C *vs*. butan-2-one (**1**) concentration.

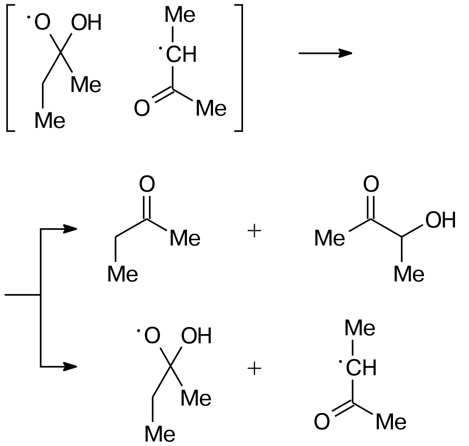
The rate constants of isomerization of EMD (k_{iso}) and its reaction with compound **1** (k_r) were calculated from the plots of k_{app} *vs*. concentration of compound **1** at different temperatures. The activation parameters of EMD isomerization to esters and the reaction of EMD with compound **1** are the following:

$$\log k_{iso} = (12.8\pm1.7) - (107\pm10)/\theta \ (r = 0.99),$$
$$\log k_r = (10.9\pm0.4) - (100\pm3)/\theta \ (r = 0.999),$$
$$\theta = 2.303RT, \text{ kJ mol}^{-1}.$$

Reaction mechanism. In the presence of oxygen at a low conversion, the main fraction of EMD is consumed molecularly or without radical escape from the solvent cage (no considerable distortions in the kinetic curves and no products of chain-radical decomposition of dioxirane, for instance, 3-(acetoxy)butan-2-one). The monomolecular route of the reaction is presented by the O—O bond homolysis to form the 2,2-bis(oxy)butylidene biradical and its subsequent isomerization (typical channel of decomposition of dioxiranes[4—10]). Since the activation energies of isomerization for biradicals of this type[27] are low, other pathways of its decomposition, such as hydrogen atom abstraction from the solvent,[28] are improbable. The bimolecular process is the reaction of solvent oxidation with dioxirane that can proceed in two parallel routes.[4] The first route leads to nonradical products, and the second route affords a radical pair in the solvent cage. This assumption is confirmed by the results of high-level quantum chemical calculations.[28,29] Thus, the processes that occur can be described by reactions (1)—(4).


(1)
(2)
(3)
(4)

The radicals formed in the solvent cage escape from it or recombine (reaction (5)) to form semiacetal, which decomposes to products identical to those obtained in the nonradical oxidation of the solvent (see reaction (3)). Further transformations involving the radicals formed proceeds as follows: in the absence of oxygen, alkyl radicals induce EMD decomposition, whereas in the presence of oxygen they are transformed into alkylperoxyl radicals that decay in recombination or give hydroperoxides. The oxygen-centered radicals undergo β-cleavage or detach the hydrogen atom from the solvent. The reactions of the 2-(2-oxobutan-3-yloxy)butan-2-yloxyl, 2-ethoxybutan-2-yloxyl, and 2-methoxybutan-2-yloxyl radicals with compound **1** were neglected because of the absence of 3-hydroxybutanone, ethanol, and methanol in the reaction products of dioxirane decomposition in deoxygenated solutions. Taking into account the above assumption, the mechanism of subsequent EMD transformation in a deoxygenated solution of compound **1** can be presented by reactions (5)—(16).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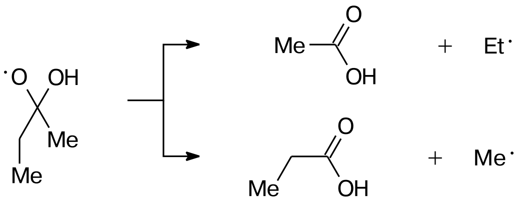
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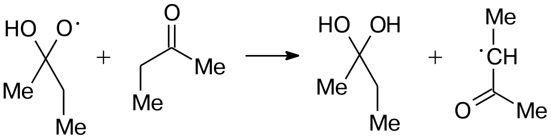
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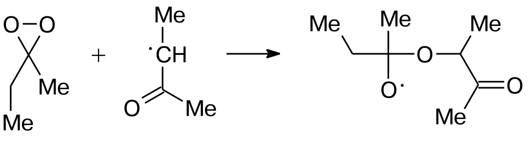
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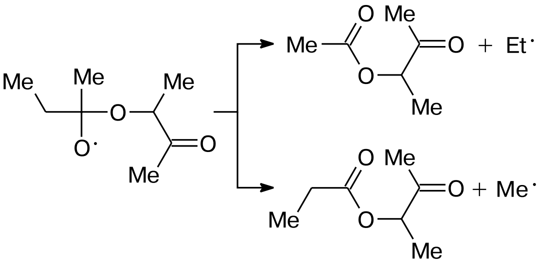
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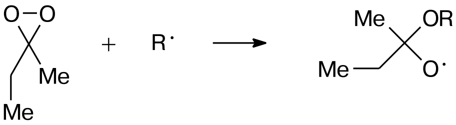
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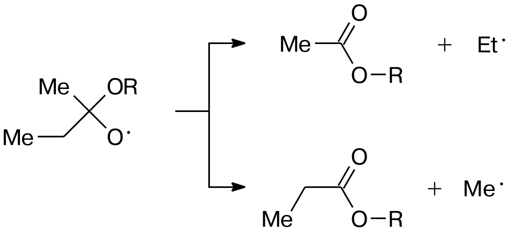
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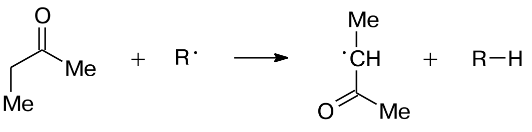

(16)

R = Me, Et

The chain-radical decomposition of dioxirane is led by the Me$^\bullet$, Et$^\bullet$, and MeC(O)C$^\bullet$(H)Me radicals, which decay in homo- and/or cross-recombination. The predomination of cross-recombination has earlier**[4]** been shown for dimethyldioxirane decomposition in acetone. It cannot be ruled out that this process is also prevailing in the present case.

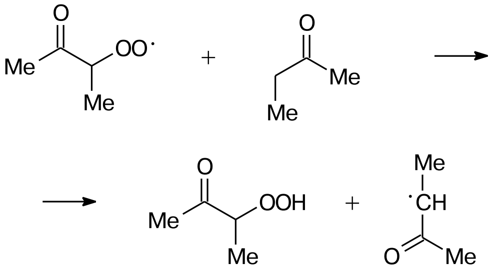
Among the presented reactions, reaction (16) should be noted. It occurs with the rate constant $1.4 \cdot 10^4$ L mol^{-1} s^{-1} (for the reaction of the methyl radical**[30]**) and should compete with reaction (13), whose rate constant can be accepted approximately equal to that of the reaction of dimethyldioxirane with the methyl radical, *i.e.*, ~10^5—10^6 L mol^{-1} s^{-1} (see Refs 31 and 32). Thus, for the methyl radical $w_{13}/w_{16} = 0.5$—0.01 under the experimental conditions, which is confirmed by the low yield of methyl esters (see Table 1). No data on the reaction rate constants necessary for analysis are available for the ethyl radical. However, based on the composition of the products, we can conclude that the both reactions should be taken into account.

The ratio of the decomposition constants of the 2-(2-oxobutan-3-yloxy)butan-2-yloxyl radical can be estimated from quantitative analysis of the products of EMD thermal decomposition in solutions of compound **1** containing no oxygen. At 50 °C the k_{11}/k_{12} ratio is 3.7±0.3. This analysis is not quite correct for other oxyl radicals, because the yield of their conversion products is low and can be determined with high error. In addition, ethyl acetate can be formed on storage of dioxirane solutions and accumulated during the induction period until complete oxygen consumption. However, the data obtained suggest that for these oxyl radicals the elimination of the ethyl group is more favorable than that of the methyl group.

In the presence of oxygen, chain termination occurs on peroxyl radicals (Eqs (17)—(19)).

$$R^\bullet + O_2 \longrightarrow ROO^\bullet \qquad (17)$$

$$ROO^\bullet + ROO^\bullet \longrightarrow Alc + Kt + O_2 \qquad (18)$$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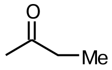
R = Me, Et, 

Alc is alcohol, Kt is ketone

In the case of butan-2-on-3-ylperoxyl radicals, chain propagation reactions can occur in the presence of oxygen (see reactions (17) and (19)), which is caused by the low reaction constant of their recombination: $1.5 \cdot 10^6$ L mol^{-1} s^{-1} at 35 °C.[26] The results of studying the reaction products (see Table 1) agree well with the above presented data. The products of initiated oxidation of compound **1** with oxygen[26] is observed, namely, ethyl acetate, acetaldehyde, and butanedione. Although the formation of some of them can be explained by the reactions involving EMD, pay attention that the yields of the products based on the consumed dioxirane is more than 100%. Therefore, in this case, oxygen is involved in solvent oxidation. In addition, the dioxirane itself cannot result in the formation of hydroperoxides.[1—3]

Methyl- and ethylperoxyl radicals are characterized by the high recombination rate and are not involved in chain propagation, because the rate constants of their square decay are by three orders of magnitude higher[33] and the rate constant of their cross-recombination with the butan-2-one-3-ylperoxyl radicals, by analogy with radicals similar in structure, should be lower than the recombination rate constant by approximately two orders of magnitude.[26,33,34]

Let us estimate the chain length involving the butan-2-on-3-ylperoxyl radicals (hereinafter ROO$^\bullet$) as the ratio of the rate of chain propagation involving these radicals to the radical decay rate

$$v = k_{19}[\mathrm{ROO}^\bullet][\mathbf{1}]/(2k_t[\mathrm{ROO}^\bullet]^2) = k_{19}[\mathbf{1}]/(2k_t[\mathrm{ROO}^\bullet]),$$

where k_t is the rate constant of homorecombination of the MeC(O)CH(OO$^\bullet$)Me radicals. Cross-recombination with the methyl- and ethylperoxyl radicals was neglected because of its low rate compared to the homorecombination rate.[34]

Using the quasi-stationarity principle with respect to the butan-2-on-3-ylperoxyl radical for the reaction in the presence of oxygen, we can write

$$[\mathrm{ROO}^\bullet] = (0.5\xi k_r C_D[\mathbf{1}]/k_t)^{0.5},$$

where C_D is the EMD concentration, ξ is the probability of radical escape into the bulk in the reaction of EMD with compound **1**, and k_r is the rate constant of this reaction. This expression was composed ignoring reaction (9), which makes no substantial contribution to the generation of the ROO$^\bullet$ radicals.[35] Substituting this expression for the ROO$^\bullet$ concentration into the formula for the chain length, we obtain

$$v = k_{19}[\mathbf{1}]^{0.5}/(2\xi k_t k_r C_D)^{0.5}.$$

Averaging the chain length from the initial concentration of dioxirane $C_D{}^0$ to the inflection point in the kinetic curve corresponding to the $C_D{}^t$ concentration gives the equation

$$\bar{v} = \frac{1}{C_D^0 - C_D^t}\int_{C_D^t}^{C_D} k_{19}\left(\frac{[\mathbf{1}]}{2\xi k_r k_t}\right)^{0.5} C_D^{-0.5}\,\mathrm{d}C_D.$$

Thus, the average chain length value in the induction period is the following:

$$\bar{v} = k_{19}\left(2\frac{[\mathbf{1}]}{\xi k_r k_t}\right)^{0.5}\frac{\left(C_D^0\right)^{0.5} - \left(C_D^t\right)^{0.5}}{C_D^0 - C_D^t}.$$

At 35 °C, $C_D{}^0 = 0.057$ mol L^{-1}, and $\Delta C_D = 8.7 \cdot 10^{-3}$ mol L^{-1}, the average chain length is 10—0.1 for $\xi = 0.1$—1, respectively ($k_r{}^{35} = 1.18 \cdot 10^{-6}$ L mol^{-1} s^{-1}; $k_t{}^{35} = 1.47 \cdot 10^6$ L mol^{-1} s^{-1};[20] $k_{19}{}^{35} = 0.14$ L mol^{-1} s^{-1} [20]). The calculated range of chain length values is rather wide, which makes it possible to use the obtained expression for the estimation of ξ with high accuracy. According to the reaction scheme, the stoichiometric inhibition coefficient for oxygen (f) is $1 + \bar{v}$. Therefore, the amount of absorbed oxygen is the following:

$$[\mathrm{O}] = \xi(1 + \bar{v})(C_D{}^0 - C_D{}^t).$$

Plotting the dependence of the calculated amount of oxygen absorbed during the induction period at different ξ values and comparing it with the solubility of oxygen in compound **1** (see above), we obtain that at 35 °C the average chain length is 1.6 and the probability of radical escape into the bulk is 0.43±0.06. Thus, the efficiency of initiation in the system under study is high and comparable with the values for substrate—dimethyldioxirane systems.[4,35]

Quantum chemical calculations. In addition to the experimental study, we performed quantum chemical calculations of the EMD thermolysis. The geometric parameters of the reactants, transition states, and intermediates of the process, as well as the corresponding activation barriers, were calculated.

In the present study, all calculations were performed using the (U)B3LYP method of the density functional theory, which describes well the decomposition of dioxiranes.[27]

A EMD molecule can exist in two conformations (Fig. 3). Conformation **B** is energetically more favorable (by 1.5 kJ mol^{-1} as shown by 6-311+G**) than **A**, although the dipolar moment of the latter (3.2 D) exceeds that for **B** (3.0 D), which should facilitate slightly a greater

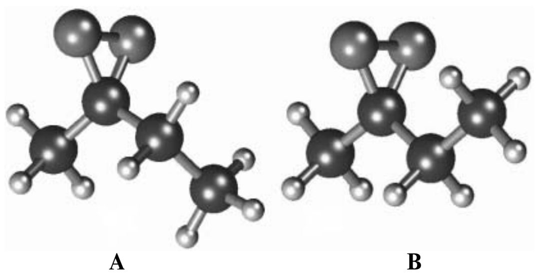


Fig. 3. Structures of conformations **A** and **B** of ethyl(methyl)dioxirane according to the B3LYP/6-311+G(d,p) theoretical data.

Table 2. Potential energy barriers and selected geometric parameters of the transition state of the O—O bond homolysis in EMD according to the UB3LYP theoretical data

Conformation	Basis set	ΔE*	μ/D	*d*/Å		
				O—O	O(1)—C	O(2)—C
A	6-31G(d,p)	118	3.14	2.054	1.354	1.355
	6-311+G(d,p)	106	3.50	2.027	1.356	1.356
B	6-31G(d,p)	120	2.96	2.064	1.353	1.353
	6-311+G(d,p)	107	3.28	2.032	1.355	1.355

* ΔE (kJ mol^{-1}) taking into account ZPE.

stabilization of conformation **A** in solution. Such a small difference in the parameters of conformers **A** and **B** and the low energy barrier (8.8 kJ mol^{-1}; B3LYP/6-31G**) for the transformation of one conformation into another indicate that the both forms exist in comparable amounts. Therefore, further calculations were performed for the both conformers.

The limiting step of dioxirane isomerization is the formation of the 2,2-bis(oxy)butylidene biradical upon the homolysis of the O—O bond. The geometric parameters of the transition state (TS) and the energy barriers were calculated by the (U)B3LYP method (Table 2). The obtained values are well consistent with the experimentally observed activation energy of the monomolecular pathway of EMD consumption. The experimental activation energy for dimethyldioxirane decomposition (75 kJ mol^{-1}; solvent acetone—CCl_4)[4] and the activation barrier calculated[21] by the UB3LYP/6-31G(d,p) method (97 kJ mol^{-1}) are lower than those for EMD. The geometry of the TS for the O—O bond homolysis in a EMD molecule is characterized by the value of the cleaved bond, which is by 0.034 or 0.044 Å (depending on the EMD conformation) greater than that for dimethyldioxirane. Based on the results of quantum chemical calculations, the authors[27] assumed that the stability enhanced with the elongation of the alkyl substituents. Our experimental and calculated data confirm this assumption.

The next step of the process is the rearrangement of the biradical to esters. Two routes of this reaction are possible: with migration of either ethyl or methyl group.

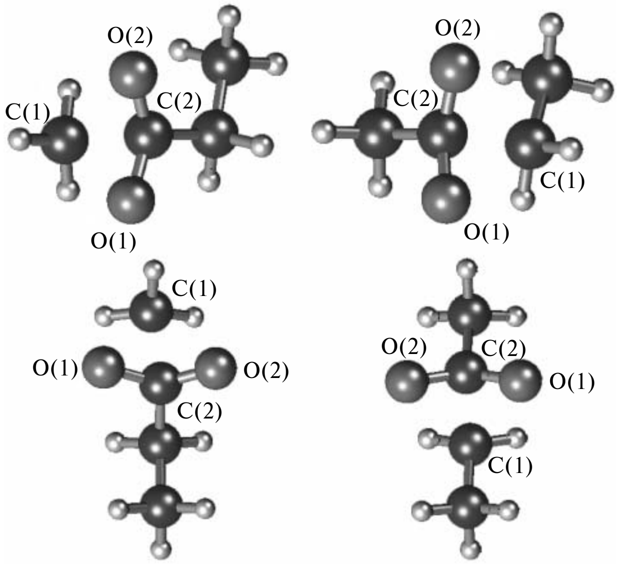


Fig. 4. Structures of the transition states of isomerization of the 2,2-bis(oxy)butylidene biradical to esters according to the UB3LYP/6-31G(d,p) theoretical data.

The geometric parameters of the TS (Fig. 4) for these pathways and the energy barriers (Table 3) were calculated. The obtained values of the barrier for the migration of the methyl group is by ~15 kJ mol^{-1} higher than those for the ethyl group. Therefore, ethyl acetate formation should be energetically more preferential, which is observed experimentally, and the major product of EMD isomerization is ethyl acetate. However, it should be taken into account that the difference between the TS of the O—O bond homolysis and the maximum energy of the biradical is ~67 kJ mol^{-1} and the energy barriers of isomerization are rather low. In the gaseous phase the process will result, most likely, in the formation of the both esters in comparable amounts, because the biradical cannot consume rapidly an excessive energy. As a consequence, the both isomerization pathways occur regardless of their activation barriers. When the reaction is carried out in the condensed phase, the energy immediately dissipates to the medium, due to which only one reaction pathway affording ethyl acetate prevails. The yield of methyl propionate should increase with the temperature increase.

Table 3. Potential energy barriers and selected geometric parameters of the transition state of isomerization of the 2,2-bis(oxy)butylidene biradical according to the UB3LYP/6-31G(d,p) theoretical data

Conformation	Type of migration	ΔE*	μ/D	*d*/Å			
				C(1)—C(2)	C(1)—O(1)	C(2)—O(1)	C(2)—O(2)
A	Me	14.2	3.29	1.805	2.172	1.321	1.290
	Et	0.5	3.46	1.753	2.306	1.321	1.318
B	Me	15.9	3.28	1.813	2.163	1.322	1.289
	Et	0.9	3.13	1.743	2.329	1.321	1.321

* ΔE (kJ mol^{-1}) taking into account ZPE.

Thus, the experimental results indicate a considerable fraction of radical processes in the system under study. Temperatures below 30 °C are most optimal when using EMD as the oxidant, and the use of inert solvents containing no easily oxidizable C—H bonds is reasonable to avoid undesirable side reactions.

The isomerization of EMD in butanone affords mainly ethyl acetate, which agrees with the results of quantum chemical B3LYP calculations.

In deoxygenated solutions of butanone, the chain-radical decomposition of dioxirane is induced by the Me$^\bullet$, Et$^\bullet$, and MeC(O)C$^\bullet$(H)Me radicals, and the contribution of the latter to this process is maximum.

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