The kinetic regularities, products, and mechanism of the thermal decomposition of dimethyldioxirane. The contribution of molecular and radical reaction channels*

S. L. Khursan, S. A. Grabovskii, N. N. Kabal'nova, E. G. Galkin, and V. V. Shereshovets*

Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences, 71 prosp. Oktyabrya, 450054 Ufa, Russian Federation. Fax: +7 (347 2) 35 6066. E-mail: chemox@anrb.ru

The products and kinetics of the thermal decomposition of dimethyldioxirane (DMDO) were studied. The reaction proceeds via three parallel pathways: isomerization to methyl acetate, oxygen atom insertion into the C-H bond of a solvent molecule (acetone), and the solvent-induced homolysis of the O-O bond in the DMDO molecule. The contribution of the latter reaction channel is ca. 23% at 56 °C. The overall kinetic parameters of DMDO thermolysis in oxygen atmosphere were determined. The free radical-induced DMDO decomposition occurs in an inert atmosphere. The formal kinetics of this reaction was investigated. The mechanism of the DMDO thermolysis is discussed.

Key words: dimethyldioxirane, thermolysis, kinetics, reaction mechanism.

Dioxiranes, three-membered cyclic peroxides, are efficient oxidants for organic compounds of various classes.¹⁻³ A distinctive chemical property of dioxiranes is a combination of the high reactivity and selectivity of oxidation reactions.⁴ The hydroxylation of saturated organic compounds, including hydrocarbons that contain inactive C-H bonds, is one of the most dramatic examples of dioxirane reactivity.

The mechanism of the interaction between dioxiranes and the C-H bond is acutely debated. It has been shown⁵ that dimethyldioxirane (DMDO, **1a**) exhibits electrophilic properties in reactions with hydrocarbons. The reaction is accelerated in the presence of protondonor solvents.⁶ It was suggested that the oxidation of the C-H bond proceeds *via* the oxygen atom insertion mechanism^{7.8} (Scheme 1).

Scheme 1



* Dedicated to Professor E. T. Denisov on the occasion of his 70th Birthday.

Dioxirane 1a reacts selectively with the C--H bond. The ratio of the oxidation rates (based on one H atom) for the primary, secondary, and tertiary C--H bonds in toluene, ethylbenzene, and cumene is 1 : 24 : 91, respectively.⁷ The reaction is characterized by moderate isotope effects: 2.2 (*cyclo*-C₆D₁₂, 1b, -23.9 °C)⁸ and 4.97 (*cyclo*-C₆D₁₂, 1a, 22 °C).⁷ The high stereospecificity of oxidation is believed to be forcible evidence for such an "oxenoid" mechanism.^{7,8}

However, along with the above facts, experimental evidences are available for the participation of free radicals in the oxidation process. Photolysis and thermolysis of dioxiranes is initiated by the radical-chain decomposition of 1a and 1b.9,10 The oxidation of cyclohexane and adamantane in the presence of CBrCl₃ resulted in halogen-containing hydrocarbons among the other reaction products.¹¹ Carbon-centered radicals formed due to interaction of la with ethers, aldehydes, and alkanes have been found with the use of inhibitors of radical processes.^{12,13} Finally, the presence of dioxygen in the system affected drastically the oxidation rate and the composition and yield of the reaction products.¹³ These facts allowed the conclusion to be drawn¹¹⁻¹³ that the interaction between dioxiranes and saturated organic compounds proceeds via the radical mechanism (Scheme 2).

An efficient intracell decay of a radical pair was assumed to be a reason for the stereospecificity of the reactions of dioxiranes with the substrate under oxidation.¹³

The data of some studies, 11-13 contradicting the common views, have been thoroughly examined and stimulated further study on the mechanism of the reaction of dioxiranes with saturated organic compounds. In

Published in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 8, pp. 1344-1354, August, 2000.

1066-5285/00/4908-1338 \$25.00 © 2000 Kluwer Academic/Plenum Publishers



particular, it has been shown¹⁴ that the interaction between CBrCl₁ and **1a** is accompanied by the generation of free radicals and halogen derivatives of adamantane are formed as by-products. Some inhibitors of radical processes (for example, 2,2,6,6-tetramethylpiperidine-1-oxyl) also initiate the radical decomposition of 1a and 1b.15 Hence, it makes no sense to use them for proving the radical nature of the interaction between dioxiranes and C-H bonds. The oxidation of (R)-2-phenylbutane by DMDO proceeds with complete maintenance of the configuration, although the radical H atom abstraction from the chiral center should be accompanied by racemization.¹⁶ The data on the oxidation of (trans-2-phenylcyclopropyl)ethane by dioxirane la can serve as additional argument in favor of the "oxenoid" mechanism.¹⁷ This reaction virtually proceeds without opening the three-membered cycle of the hydrocarbon (Scheme 3).

The ratio between the overall yield of the products 4 + 5 + 6 and 2 + 3 is ~3%. Acetate 7 also forms as traces. The oxidation of cyclohexane by dioxirane 1a in a solution and in the gas phase has been studied.¹⁸ In both cases, cyclohexanone was the main reaction product.

Nevertheless, the discussion is far from completion. The authors of the radical mechanism have thoroughly examined their findings and those of the opponents and



presented new evidences on the participation of free radicals in the hydrocarbon oxidation.¹⁹ For example, cyclohexene epoxide, which was found in the products of cyclohexane oxidation.¹⁸ can be formed only from cyclohexene that was an intermediate in the radical process¹⁹ (Scheme 4).

The participation of radicals in the reaction of cumene with dioxirane **1a** has been observed.²⁰ The reaction is accompanied by chemiluminescence in the visible region of the spectrum, indicating the presence of free radicals in the system. This reaction leads to dimethylphenylcarbinol and acetophenone in the ratio typical of radical-chain cumene oxidation.

Thus, the main arguments of the opposite sides are the following.

"Oxenoid" mechanism. The interaction of dioxiranes with saturated organic compounds proceeds via the mechanism of O atom insertion into the C—H bond^{14,16} if the factors capable of initiating the radical-chain oxidation are absent: additives of active substances, traces of transition metals, micro-admixtures, the effect of luminous radiation, the presence of oxygen in a solution, etc.

Radical mechanism. The substrate molecules induce the homolysis of the O–O bond in the dioxirane mole-



Scheme 3

Atmosphere	<i>T</i> ∕°C	Yield of the product ^a				
		CH ₃ COOCH ₃	СН,СОСН,ОН	CH ₃ COOCH ₂ COCH ₃	СН ₃ СООН	
0 ₁	10	0.98	0.02			
0	50	0.59	0.39		0.02	
O_{2}^{2b}	50	1			—	
Ar	41	Traces	Traces	1	Traces	

Table 1. The products of DMDO thermolysis (acetone is the solvent)

^a Calculated per consumed 1a.

^b The solvent is CCl₄.

cule.¹⁹ The H atom abstraction by the bis-oxyisopropylidene biradical formed results in the radical cell pair, which undergoes fast cross-recombination. A small fraction of radicals evolves into the bulk of a solvent, initiating the radical-chain dioxirane decomposition.

The study of the kinetic features of the process is one of the methods for studying mechanisms of the chemical transformations. Previously, the kinetics of DMDO decomposition in a oxygen atmosphere²¹⁻²³ and its reactions with hydrocarbons (cumene,²⁰ 2-methylbutane,²⁴ and adamantane²⁵) have been studied. The free-radical processes have been found to play an important role in these reactions. In this work, the effect of oxygen on the kinetic features and the products of the DMDO thermal decomposition, as well as the relationship between molecular and radical pathways of its consumption, is studied.

Experimental

Acetone (high purity grade) was purified by distillation. Hydrocarbons (chemically pure), 2,2,4-trimethylpentane, *n*-octane, and cyclohexane were treated with concentrated H_2SO_4 , dried over Na, and distilled on a Fischer Mikro-SPALTROHR® distillation column. The purity of reagents was tested by GLC (a Chrom 5 chromatograph, 3.7 m × 3 mm column, SE-30) and the UV absorbance spectra.

Dioxirane 1a^{26,27} was synthesized according to a known procedure²¹; it was identified and analyzed according to the earlier described method.³ Water admixtures were removed by freezing (an acetone-liquid nitrogen cooling mixture). Dehydration of the la solutions with magnesium sulfate results in a sharp decrease in the lifetime of dioxirane. The kinetics of la decay in acetone, CCl₄, and binary solvents were monitored spectrophotometrically (Specord M-40) by a decrease in absorbance ($\lambda = 335$ nm) in the temperature range of 24-56 °C. The reactor was a thermostatted quartz cuvette (volume 1.1 mL, optical path 0.5 cm). The starting concentration of la was varied in the (2.7-11.1) · 10⁻² mol L⁻¹ range. Oxygen or argon was purged through the la solution prior to experimental runs. It was shown in preliminary experiments that the content of la remained virtually constant. The concentrations of O₂ in acetone and in the binary acetone-hydrocarbon systems were calculated from the published data²⁸ assuming molar additivity. The reaction products were analyzed on a chromatographmass-spectrometer-computer system; a Hewlett Packard HP-5980 chromatograph with an HP-5972A mass-selective detector (column 50 m × 0.2 mm; Ultra-2; grafted phase, methylsilicon rubber: carrier gas, helium) and by the ¹H NMR spectra recorded on a Bruker AM-300 spectrometer with a working frequency of 300 MHz (acetone-d6 and CCl4 as solvents, Me4Si as the internal standard).

Results and Discussion

Reaction products. The composition of the products of **1a** thermal decomposition depends on the O_2 concentration in the solution and the temperature. The results of chromato-mass-spectrometric analysis of the solution under study after the reaction (complete consumption of **1a**) are presented in Table 1. When **1a** decomposed in the presence of O_2 at 10 °C, methyl acetate was the only reaction product. When **1a** decomposed at 50 °C, the fraction of methyl acetate in the total products decreased to 59%; 39% of 1-hydroxypropan-2-one (acetol) and 2% of acetic acid also formed. Quite another picture was observed when O_2 was removed by purging the solution of **1a** with argon. Acetol acetate CH₃COOCH₂COCH₃ was the main reaction product at 41 °C; traces of methyl acetate and acetol were also found.

To elucidate the effect of acetone on the mechanism of thermal decomposition of 1a, the decomposition of dioxirane in an inert solvent CCl_4^* was studied. With this purpose, 1a was extracted by tetrachloromethane from a solution in acetone according to the previously published procedure.²⁹ The solution obtained was washed 3 times with water, and the latter was then removed by freezing. As a result, 0.11 *M* solution of 1a in CCl_4 (according to the data of iodometric titration) containing less than 0.15 mol L⁻¹ of acetone was obtained. Thermal decomposition of 1a was carried out at 50 °C in an O₂ atmosphere for 24 h. After the procedure was completed, a small amount of unreacted dioxirane was found in the solution. The ¹H NMR method showed the presence of methyl acetate as the only reaction product.

The findings on the reaction products in the solutions saturated with O_2 give evidence of parallel occurrence of two processes, monomolecular conversion of 1a into methyl acetate and reaction between dioxirane and acetone. The latter reaction is suppressed at 10 °C due to a high strength of the primary C-H bond in the acetone molecule, and the yield of acetol is minimum (2%). When the temperature increases, the involvement of the solvent in the 1a thermal decomposition becomes more probable. In this case, the reaction likely proceeds through both oxygen atom insertion and radical mecha-

^{*} Because of the low strength of the O—Cl bond, the abstraction of a Cl atom by the oxyl radical or the molecular insertion of an O atom into the C—Cl bond is thermodynamically unfavorable.

nisms. The formation of acetic acid gives evidence in favor of this assumption (see Table 1).

The mechanism of the methyl acetate formation has been studied.³⁰ Ab initio calculations by the B3LYP/6-31G(d, p) method indicate that methyl acetate forms as a result of isomerization of the bisoxyisopropylidene biradical (Scheme 5).





It was found that the activation barrier of the isomerization of the biradical into methyl acetate is only 3.8 kcal mol⁻¹. The decomposition of the biradical (or **1a**) to CO₂ and ethane is highly energy consuming. Therefore, it cannot compete with the rearrangement to the ester.³⁰

The reaction kinetics in an oxygen atmosphere. Thermal decomposition of 1a in an acetone solution saturated with oxygen proceeds slowly. At 40 °C, the 1a conversion at 10⁴ h is only 13%. The first kinetic order with respect to dioxirane was observed. The effective rate constant of the 1a thermal decomposition, $k_{\rm eff}$, is independent of its concentration. A decrease in the acetone concentration (diluted with tetrachloromethane) lowers $k_{\rm eff}$ it was found at 50 °C:

$$k_{\rm eff}$$
 (s⁻¹) = 1.8 · 10⁻⁵ + 1.5 · 10⁻⁶[CH₃COCH₃].



Fig. 1. Typical kinetic curves for DMDO consumption. Conditions: acetone is the solvent, 50 °C, previous purging of the solution with oxygen (a) or argon (b). The results of processing the kinetic curves according to the first-order equation and Eq. (42) are shown by solid lines (1, 2 and 3, respectively).

This regularity is in line with the conclusion on the competition between the mono- and bimolecular channels of **la** consumption, which was drawn from analysis of the products.

Purging with argon for 2 min decreases the O_2 concentration in the solution. This results in a sharp acceleration of the reaction upon the complete consumption of O_2 (Fig. 1). However, before this moment, the reaction rate remains the same as in the experiments in which the presence of O_2 in the solution was maintained during the whole kinetic run.

The temperature effect on the k_{eff} values is shown in Fig. 2. The activation parameters for the **la** decomposition (acetone is the solvent) were determined from these data:

$$\log k_{\rm eff} = (10.2 \pm 0.6) - (21.6 \pm 0.9)/\theta$$

r = 0.992, $\theta = 2.3RT$ kcal mol⁻¹. The k_{eff} values found are in good agreement with the published data²¹ (see Fig. 2). Thermolysis of DMDO in CCl₄ proceeds somewhat slower; the effective rate constants depend on the temperature as follows (CCl₄ is the solvent):

$$\log k_{\rm eff} = (7.1 \pm 0.3) - (18.0 \pm 0.5)/\theta.$$

The retardation of the reaction is due to the absence of C-H bonds. Hence, isomerization to methyl acetate is the main channel of **1a** consumption. This assumption is in line with both the data for k_{eff} (at 50 °C $k_{eff} = 1.7 \cdot 10^{-5} \text{ s}^{-1}$) and the results of analysis of the reaction products. The homolysis of the O-O bond in the **1a** molecule is the rate-determining stage of isomerization, which is characterized, according to the data of



Fig. 2. Temperature dependence of the effective rate constant of dimethyldioxirane consumption in the presence of oxygen. The k_{eff} values were determined either during the induction period (1) or for the total consumption of dioxirane after previous purging of the solution with oxygen (2). The dependence found previously²¹ is shown by the dash line.

the B3LYP/6-31G(d, p) calculation, 30 by an energy barrier of 23.1 kcal mol⁻¹, *i.e.*, ~5 kcal mol⁻¹ higher than the experimental activation energy.

The rate of DMDO thermal decomposition is affected significantly by trace contaminations that were introduced during the synthesis and separation of dioxirane.²² Previously,^{20,22–24} we have repeatedly studied the kinetics of **1a** thermolysis. Reproducible k_{eff} values were obtained only when we gave up the drying with magnesium sulfate or potassium carbonate and storage of la over molecular sieves, although these procedures are commonly used.^{3,6,8}. We removed water admixtures by freezing the solution. High purity of dioxirane is necessary in cases when oxidation is slow. On the other hand, the presence of trace contaminations initiates the radical decomposition of dioxiranes and can serve as the origin of errors in the interpretation of the kinetic data and mechanism of the interaction of la and 1b with substrates of oxidation.

The fraction of the radical channel of DMDO consumption. The complete consumption of O_2 from the saturated solution at 50 °C occurs in $-5 \cdot 10^3$ s. The removal of O_2 by Ar decreases the induction period (see Fig. 1). A sharp acceleration of the reaction (by a factor of 50-100) indicates a change in the mechanism of DMDO consumption. It has firmly been found^{11,20,24} that the high reaction rate is due to free radical-induced 1a decomposition. This process begins when the O_2 concentration in the solution decreases insomuch that it cannot trap allyl radicals. Taking into account³¹ that the rate constant for the $R^* + O_2$ reaction is high $((1-5) \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1})$, one can treat the sharp acceleration of dioxirane decomposition as evidence for the complete consumption of O₂. The system under study is a typical example of the complete inhibition of the radical-chain process, and O2 is the efficient acceptor of free radicals. The theory of chain processes inhibition has been studied in detail.³² According to its main concepts, the O₂ consumption rate is proportional to the initiation rate* and the efficiency of initiation due to the decomposition of the initiator, dioxirane, can be found from the amount of the inhibitor, dioxygen, consumed.

The stoichiometry of the consumption of 1a and O_2 can be determined as follows. Decomposition of one dioxirane molecule in fast successive reactions produces two carbon-centered radicals. The latter add two O_2 molecules and undergo recombination, recovering one O_2 molecule. At higher conversions of oxygen, the chains are terminated by the cross reaction

 $R' + ROO' \rightarrow ROOR$

without dioxygen evolution. Thus, the equimolar stoichiometry of the consumption of DMDO and O_2 in the

radical channel of la thermal decomposition is maintained during the whole induction period. Hence, the $[O_2]/\Delta[DMDO]$ ratio (where $\Delta[DMDO]$ is the amount of dioxirane decomposed during the induction period, see Fig. 1) is the fraction of the processes leading to free radicals formation in the overall channel of DMDO consumption. According to Fig. 1, 0.020 mol L^{-1} of dioxirane decomposed during the induction period at 50 °C. The O_2 concentration in acetone at this temperature is equal²⁸ to 0.004 mol L^{-1} ; hence, the fraction of the radical channel $\xi = [O_2]/\Delta[DMDO] = 20\%$. A similar approach can likely be applied to the reaction of 1a with organic substrates. Table 2 shows the ξ values for a series of hydrocarbons. One can conclude that the initiation efficiency in the dioxirane-hydrocarbon system is high. This fact is in line with the conclusion¹⁹ on the hydrocarbon-induced homolysis of the O-O bond in the dioxirane molecule and is an argument in favor of the radical mechanism of the reaction of la with the C-H bond.

The reaction kinetics in the absence of O_2 . A study of the kinetics of the radical-chain-induced decomposition of 1a revealed the following features. The kinetic curve can be described by an exponent with reasonable accuracy. However, a small but well reproducible deviation of the effective reaction order with respect to dioxirane (n) from unity was observed. The optimization of the reaction order with respect to 1a by the integral method results in an n value from 1.0 to 1.5 for various experimental conditions of chain decomposition. When the rate of 1a decomposition is described by a first-order equation, the rate constant k_{ch} depends linearly on the DMDO concentration (Table 3). The dependence of the initial rate of the 1a induced decomposition (w_0) on [DMDO]₀ at the portion of the kinetic curve immedi-

Table 2. The ratio between the molecular and radical channels of the reaction of DMDO with organic compounds^a

Substrate	[RH]0	[DMDO] ₀	<i>T/</i> °C	[0 ₂]/Δ[DMDO]
	mol	L-1		(%)
Acetone	13.6	0.108	50	20
	13.6	0.096	56	23
2,2,4-Tri-	0.61	0.061	41	68
methylpen-	0.83	0.083	41	76
tane	0.99	0.079	41	73
	1.1	0.078	41	76
	1.2	0.075	41	71
	1.7	0.070	25	57
n-Octane	0.84	0.077	41	51
	1.2	0.071	41	53
Cyclo-	1.7	0.078	41	66
2-Methyl- butane ^b	0.52-4.6	0.019-0.071	25	50

^a The concentration of O_2 in solutions was calculated from the literature data.²⁸

^b See Ref. 24.

^{*} The initiation rate does not include the contribution of latentradical processes. According to previous studies, ¹⁹ fast intracage recombination of the radical pair is a distinct feature of the radical mechanism of the reaction between dioxiranes and hydrocarbons.

(DMDO] ₀ ^a /mol L ⁻¹	$k_{\rm ch} \cdot 10^3/{\rm s}^{-1}$	$w_0^{b} \cdot 10^5 / \text{mol } \text{L}^{-1} \text{ s}^{-1}$	$k^{(1)} \cdot 10^3/\mathrm{s}^{-1}$	$k^{(2)} \cdot 10^2 / \text{L moi}^{-1} \text{ s}^{-1}$
0.101	2.1	9.48	2.0	0.4
0.102 ^d	3.5	16.8	3.2	2.0
0.026	1.5	2.96	1.4	2.7
0.041	2.2	6.29	1.4	4.1
0.055	2.4	8.53	1.8	3.4
0.077	3.1	13.6	3.1	1.8
0.092	4.1	16.8	3.3	4.1
0.102	3.6	19.0	3.0	2.8
			2.5±0.3	3.2 ± 0.4

Table 3. Kinetic parameters of the radical-chain decomposition of 1a (acetone, 50 °C)

^a The DMDO concentration corresponding to the inflection point on the kinetic curve (for example see Fig. 1). ^b The rate in the initial portions of the chain consumption of 1a.

^c At 41 °C.

AL 41 C.

^d At 45 °C.

ately after inflection (see Table 3) results in a similar conclusion. The plots of w_0 versus $[DMDO]_0$ and of $w_0/[DMDO]_0$ versus $[DMDO]_0$ are linear. These formal-kinetics features lead to the conclusion that the main amount of **1a** is consumed in a reaction of the first order with respect to dioxirane. However, a minor reaction channel that is characterized by a higher (apparently, second) reaction order with respect to DMDO also manifests in the kinetics.

The reaction mechanism. As shown above, in the presence of dissolved O_2 , the main fraction (~80%) of DMDO is consumed by the molecular pathway or at least without evolution of radicals from the solvent "cell." We examined three versions of the reaction: O atom insertion into the C-H bond, homolysis of the O-O bond induced by the substrate of oxidation, and monomolecular homolysis of the O-O bond. The first two types of reactions are bimolecular, and one can suggest that they proceed through an intermediate complex of dioxirane with acetone. The latter can either transform into acetol, regenerating acetone (insertion mechanism) or form a radical cell pair (radical mechanism). This assumption was confirmed by the findings of recent high-level quantum-mechanical calculations,³³ which showed that the reaction of dioxirane with the C-H bond proceeds through a transition state of the O atom insertion type. The decay of the transition state results in either alcohol or a radical pair. Similar conclusions have been drawn by several researchers.14,16,17 The monomolecular homolysis of the O-O bond leads to bis-oxyisopropylidene biradical. Due to the low activation energy of its isomerization to methyl acetate,³⁰ other channels of its consumption such as destruction or H atom abstraction from an acetone molecule are improbable. These processes can be described as the following sequence of reactions:

$$>_{0}^{0}$$
 + ch₃coch₃ \longrightarrow K, (+1)(-1)

$$\Box \rightarrow CH_3COCH_2OH + CH_3COCH_3$$
(2)

$$\begin{array}{c} \mathsf{K} \xrightarrow{\mathsf{OH}} \\ & \\ \mathsf{O} \xrightarrow{\mathsf{OH}} \cdot \mathsf{CH}_2\mathsf{COCH}_3 \end{array} \right], \tag{3}$$

$$\searrow_{0}^{0} \rightleftharpoons \searrow_{0}^{0}$$
, (+4)(-4)

$$\searrow_{0}^{0} \longrightarrow CH_{3}COOCH_{3}$$
 (5)

Further transformations of the radical intermediates proceed as follows: the alkyl radicals react with O_2 or, in its absence, induce **1a** decomposition and decay by recombination. The oxygen-centered radicals undergo β -cleavage or H atom abstraction from the acetone molecule:





$$CH_{3}COCH_{2}^{\cdot} + \underbrace{\searrow_{1}^{0}}_{0} \longrightarrow \underbrace{\bigcirc_{0}^{OCH_{2}COCH_{3}}}_{0}, (10)$$

$$\xrightarrow{\text{OCH}_2\text{COCH}_3} \xrightarrow{\text{OCH}_2\text{COCH}_3} \xrightarrow{\text{OCH}_2\text{COCH}_3} (11)$$

$$\sim$$
 $^{\text{OCH}_2\text{COCH}_3}$ + CH₃COCH₃ \rightarrow

$$\rightarrow$$
 CH₃COCH₃ + CH₃COCH₂OH + CH₃COCH₂, (12)

$$CH_3 + \bigvee_{0}^{0} \longrightarrow \bigvee_{0}^{0CH_3}$$
, (13)

$$\searrow_{0}^{\text{OCH}_3} \longrightarrow \text{CH}_3 + \text{CH}_3\text{COOCH}_3,$$
 (14)

$$\xrightarrow{\text{OCH}_3} + \text{CH}_3\text{COCH}_3 \xrightarrow{} \xrightarrow{} \text{CH}_3\text{COCH}_3 + \text{CH}_3\text{OH} + \text{CH}_3\text{COCH}_2^{-},$$
(15)

$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_3COCH_2'.$$
(16)

In the above sequence, reaction (16) proceeds¹⁹ with a rate constant of $2.7 \cdot 10^3$ L mol⁻¹ s⁻¹ and is capable of competing with reaction (13) as $k_{13} \approx 10^5$ — 10^6 L mol⁻¹ s⁻¹ .^{11,20,24} The ratio between the concentrations of acetone (13.6 mol L⁻¹) and **1a** (~0.01— 0.1 mol L⁻¹) is ~10²—10³.

In the presence of O_2 , chain termination occurs on the peroxy radicals according to the Russell scheme.³⁴ Radicals 'CH₃ and CH₃COCH₂' conduct **1a** chain decomposition and decay *via* three pathways: two *homo*recombinations and one *cross*-recombination:

$$CH_3COCH_2^{\bullet}$$
 (or CH_3) + $O_2 \longrightarrow ROO^{\bullet}$, (17)

ROO' + ROO'
$$\longrightarrow$$
 alcohol + ketone + O₂, (18)

$$CH_{3}COCH_{2} + CH_{3} \longrightarrow CH_{3}COCH_{2}CH_{3}, \qquad (20)$$

$$CH_3 + CH_3 \longrightarrow CH_3CH_3.$$
 (21)

The kinetic analysis of the mechanism. O_2 atmosphere. In this case, the rate of 1a decomposition is equal to:

$$-d[DMDO]/dt = w_{DMDO} = k_1[CH_3COCH_3][DMDO] - k_{-1}[C] + k_4[DMDO] - k_{-4}[BR].$$
(22)

where [C] and [BR] are the concentrations of the complexes of DMDO with acetone and biradical, respectively. A quasi-steady-state approximation with respect to [C] and [BR] leads to the expression

$$w_{DMDO} = ((\alpha_M + \alpha_R) \cdot k_1 [CH_3COCH_3] + + \beta_{iso} \cdot k_4) [DMDO] = k_{eff} [DMDO], \qquad (23)$$

where $\alpha_{\rm M} = k_2/A$ and $\alpha_{\rm R} = k_3/A$ are the fractions of the molecular and radical channels of the transformation of complex C, $A = k_{-1} + k_2 + k_3$; $\beta_{\rm iso} = k_5/(k_{-4} + k_5)$. Eq. (23) is in line with the first order with respect to the **Ia** concentration, which was found experimentally. The proportionality between $k_{\rm eff}$ and acetone concentration can also be explained (*cf.* the above equation for $k_{\rm eff}$ and Eq. (23)).

The analysis of the reaction products confirms the above scheme. At low temperatures, dioxirane decomposes mainly according to reactions (4) and (5), leading to methyl acetate with nearly 100% yield. At 50 °C, the major part of the products is formed by bimolecular reaction (1). Acetol forms at stages (2) and (6), and acetic acid is the product of destruction of α -oxyisopropylidene radical according to reaction (8). The molecular channel of **1a** decay apparently prevails (see Table 2), *i.e.*, $\alpha_{\rm M} > \alpha_{\rm R}$.

The contribution of the radical reaction channel (5) and the ratio between the rates of the main pathways of **Ia** decomposition, monomolecular (w_{iso}) and O atom insertion at the C-H bond in acetone (w_M), can be evaluated from the data obtained. At 50 °C (acetone is the solvent), $k_{eff} = 3.8 \cdot 10^{-5} \text{ s}^{-1}$, and the specific rate of the homolytic reaction channel is $k_R[CH_3COCH_3] =$ $8 \cdot 10^{-6} \text{ s}^{-1}$ and $k_R = 6 \cdot 10^{-7} \text{ L} \text{ mol}^{-1} \text{ s}^{-1}$. According to the experimental data, $k_{iso} = 1.8 \cdot 10^{-5} \text{ s}^{-1}$ and $k_M =$ $(1.5 - 0.6) \cdot 10^{-6} = 9 \cdot 10^{-7} \text{ L} \text{ mol}^{-1} \text{ s}^{-1}$. Thus, in CCl₄ (acetone concentration ~1 mol L⁻¹), $w_{iso} : w_M = 1 : 0.05$, and this is in line with the high yield of methyl acetate. In acetone solutions (13.6 mol L⁻¹), $k_M[CH_3COCH_3] =$ $1.2 \cdot 10^{-5} \text{ s}^{-1}$ and the ratio $w_{iso} : w_M = 0.6 : 0.4$; this finding is in good agreement with the data of Table 1. Eq. (23) can be rewritten as follows:

 $w_{DMDO} = k_{ef} [DMDO] = (k_{ef} + k_{ef})^{2}$

$$+ (k_{\rm M} + k_{\rm R})[\rm CH_3COCH_3])[\rm DMDO], \qquad (23a)$$

where $k_{iso} = \beta_{iso} \cdot k_4$, $k_M = \alpha_M \cdot k_1$, $k_R = \alpha_R \cdot k_1$. As mentioned above, the rate constant of **1a** thermolysis in

CCl₄ is the rate constant of DMDO isomerization to methyl acetate k_{iso} . With the use of the experimental expressions for k_{eff} and ξ (see Table 2), the Arrhenius parameters for the rate constants of the radical and molecular reactions of DMDO with acetone were evaluated: $\log k_{\rm R} = 11.9 - 26.8/\theta$ and $\log k_{\rm M} = 9.5 - 23.0/\theta$, $\theta = 2.3RT$ kcal mol⁻¹.

A similar estimation was carried out for the reaction of DMDO with 2,2,4-trimethylpentane. The reaction is characterized by the first order with respect to both reactants. The rate constants of the second order, which are equal to $2.08 \cdot 10^{-5}$ L mol⁻¹ s⁻¹ at 25 °C and $1.03 \cdot 10^{-4}$ L mol⁻¹ s⁻¹ at 41 °C, were found from the experimental data. Taking into account the ξ values (see Table 2), it was found: $\log k_{\rm R} = 11.1 - 21.8/\theta$ and $\log k_{\rm M} = 4.0 - 12.3/\theta$. Note that the preexponential factors of the rate constants of the reactions of DMDO with acetone and 2,2,4-trimethylpentane through the radical direction are close to each other (taking into account the statistical correction for six C-H bonds in acetone). The difference in the activation energies of these reactions (5 kcal mol^{-1}) reflects the difference in the strength of the attacked bond in the acetone and 2,2,4-trimethylpentane molecules.

It was of interest to find a relationship between the overall rate of DMDO consumption and the rates of initiation w_i and oxygen absorption w_{O_2} . Since we used easily oxidizable hydrocarbons with a tertiary C atom, we can estimate initially the amount of consumed dioxygen due to the radical-chain oxidation of a hydrocarbon by the example of 2,2,4-trimethylpentane. The rate of the radical-chain consumption of O₂ is $w_{ch} = k_p/(2k_1)^{1/2} \cdot [RH] \cdot (w_i)^{1/2}$. For the sake of reliability, let us accept that the rate of initiation is equal to the initial reaction rate and is constant over whole induction period. At [RH] = 0.99 mol L^{-1} and [DMDO] =0.079 mol L⁻¹, the initiation rate $w_i = 8 \cdot 10^6$ mol L⁻¹ s⁻¹ (41 °C). The parameter of oxidizability is $k_{\rm p}/(2k_{\rm t})^{1/2}$ = $8.7 \cdot 10^{-5} L^{1/2} mol^{-1/2} s^{-1/2}$ (the data for the more oxidizable 2,4,6-trimethylheptane³⁵). Hence $w_{ch} =$ $2.4 \cdot 10^{-7}$ mol L⁻¹ s⁻¹, *i.e.*, 35 times lower than the rate of initiation w_i . The induction period in the conditions of our experiments was 1400 s; hence, $\Delta[O_2] = w_{ch} \cdot \tau =$ $3.4 \cdot 10^{-4}$ mol L⁻¹, *i.e.*, -5% of the initial concentration of dissolved O₂. A similar estimation for cyclohexane shows that the amount of O2 consumed during the radical-chain oxidation of hydrocarbon is <1% of the amount of O_2 consumed during the induction period. Hence, the role of these processes in DMDO thermal decomposition in pure acetone is negligible. Ignoring the contribution of the chain oxidation of hydrocarbons to the rate of O_2 consumption, we obtain

$$2w_{O_2} = w_i = w_{Ac} + w_{Me} = d[CH_3COCH_2]/dt + d[CH_3]/dt.$$
(24)

where w_{Ac} and w_{Me} are the rates of generation of acetonyl and methyl radicals, respectively. The obvious equations can be deduced from the sequence of the stages which present the mechanism of free radical generation in the system ((1), (3), (6)-(9)):

$$w_{Ac} = (1 + \delta_A) \cdot \gamma \alpha_R k_1 [CH_3 COCH_3] [DMDO], \qquad (25)$$

$$w_{Me} = \delta_A \gamma \alpha_R k_1 [CH_3 COCH_3] [DMDO], \qquad (26)$$

$$w_i = 2\gamma \alpha_R k_1 [CH_3 COCH_3] [DMDO], \qquad (27)$$

where γ is the probability of the escape of the radical pair from a "cell" of the solvent that is equal to $k_7/(k_6 + k_7)$; $\delta_D = k_8/D$ and $\delta_A = k_9[CH_3COCH_3]/D$ are the contributions of the decomposition and H atom abstraction by the α -oxyisopropyloxyl radical, $\delta_A + \delta_D = 1$, $D = k_8 + k_9[CH_3COCH_3]$.

When **1a** reacts with hydrocarbons, the rate of dioxirane consumption and the efficiency of the initiation of the radical channel increase substantially (see Table 2). This indicates that reaction (4) does not contribute significantly to the kinetics of the process. Otherwise, the reaction mechanism does not change. Hence, the rates of consumption of dioxygen and **1a** are the following:

$$w_{O_2} = 0.5w_i = \gamma \alpha_R k_i [RH] [DMDO], \qquad (28)$$

$$w_{\text{DMDO}} = (\alpha_{\text{M}} + \alpha_{\text{R}}) \cdot k_{1} [\text{RH}] [\text{DMDO}].$$
(29)

The $[O_2]/\Delta[DMDO]$ ratio is equal to that of the rates determined by Eqs. (28) and (29):

$$\zeta = \frac{[O_2]}{\Delta[DMDO]} = \frac{\gamma \cdot \alpha_R}{\alpha_M + \alpha_R} = \frac{\gamma \cdot k_3}{k_2 + k_3} = \gamma \cdot \varepsilon, \quad (30)$$

where ε is the probability of the reaction of DMDO with a hydrocarbon through the radical mechanism.

According to Eq. (30), the ξ value is independent of the concentrations of dioxirane and substrate under oxidation; this is in agreement with the experimental data (see Table 2). The contribution of radical processes is likely determined by the nature of reactants and the temperature. Eq. (30) can be recommended as a criterion of the radical pathway in the reaction between dioxirane and a compound studied. In fact, the rate of hydroxylation of the substrate is equal to

$$d[\text{ROH}]/dt = w_{\text{ROH}} = [\alpha_{\text{M}} + (1 - \gamma)\alpha_{\text{R}}] \cdot k_{1}[\text{RH}][\text{DMDO}].$$
(31)

This equation can easily be presented as

$$\mathbf{v}_{\mathsf{ROH}} = (1 - \gamma \varepsilon)(\alpha_{\mathsf{M}} + \alpha_{\mathsf{R}}) \cdot k_{1}[\mathsf{RH}][\mathsf{DMDO}] =$$

= (1 - \gamma \varepsilon) \mathbf{w}_{\mathsf{DMDO}} =
= (1 - [O_{2}]/\Delta[\mathsf{DMDO}])[\mathsf{DMDO}]. (32)

When Eq. (32) was derived, the formation of ROH in the reactions of the radicals escaped into the solvent bulk was ignored. The data of Table 2 give evidence that the reaction of DMDO with aliphatic hydrocarbons proceeds in fact through the radical pathway. We cannot rule out that the reaction is completely homolytic ($\varepsilon = 1$) and the initiation efficiency is lowered by intracell recombination (reaction (6)).

The kinetic analysis of the mechanism. Ar atmosphere. The complete removal (by purging or chemical bonding) of O_2 transforms the reaction into the regime of **1a** radical-chain decomposition. This process involves the stages of initiation (1)--(9), propagation (10)--(16), and chain termination (19)--(21), To simplify the kinetic analysis, we ignored the contribution of reactions (12) and (15) on the basis of the following considerations.

1. Acetol is virtually absent from the reaction products at 41 °C, and this fact indicates a negligible contribution of reaction (12). Notably, the kinetics of 1a chain decomposition was studied mainly at 50 °C.

2. The decomposition of α -alkoxyisopropyloxyl radical likely proceeds faster than the β -cleavage of *tert*butoxyl radical. A polar substituent destabilizes the radical and, oppositely, stabilizes the carbonyl compound that is the product of decomposition. The heat effect of the reaction

 $(CH_3)_3CO' \longrightarrow CH_3COCH_3 + 'CH_3$

is +6 kcal mol⁻¹, whereas the β -cleavage of (RO)(CH₃)₂CO[•] is characterized²⁰ by $\Delta H^0 = -5.9$ (R = CH₃) and -14.3 kcal mol⁻¹ (R = cumyl).

3. H atom abstraction from the primary C—H bond in the acetone molecule is hampered because of the high strength of the bond broken and the deactivating effect of the carbonyl group. Similarly to the reactivity of $(CH_3)_3CO^2$, one can assume that k_{12} and $k_{15} \approx$ $10^4 \text{ L} \text{ mol}^{-1} \text{ s}^{-1}$ (Refs. 36, 37). If k_{11} and $k_{14} \approx 10^6 \text{ s}^{-1}$ (values close to the rate constant of the β -cleavage of the cumyloxyl radical), then the conditions of $w_{11} >> w_{12}$ and $w_{14} >> w_{15}$ are fulfilled and ignoring reactions (12) and (15) is kinetically justified.

The rate of **1a** consumption, w_{DMDO} . is determined as follows:

$$w_{\text{DMDO}} = k_{10}[\text{CH}_3\text{COCH}_2][\text{DMDO}] + k_{13}[\text{CH}_3][\text{DMDO}].$$
 (33)

Under the quasi-steady-state approximation for the concentrations of carbon-centered radicals, we obtain

$$d[CH_{3}COCH_{2}]/dt = w_{Ac} - k_{10}[CH_{3}COCH_{2}][DMDO] + k_{16}[CH_{3}][CH_{3}COCH_{3}] - w_{LAc} = 0, \quad (34)$$

$$d[CH_3]/dt = w_{Me} + k_{10}[CH_3COCH_2][DMDO] - k_{16}[CH_3][CH_3COCH_3] - w_{t,Me} = 0, \quad (35)$$

where w_{Ac} and w_{Me} are determined by Eqs. (25) and (26); $w_{t,Ac}$ and $w_{t,Me}$ are the rates of the CH₃COCH₂⁺ and 'CH₃ radicals decay, respectively. The equation for w_{DMDO} containing the rate constants of distinct stages and concentrations of acetone and dioxirane is rather awkward for practical use. Therefore, we shall consider only qualitative correspondence of the reaction mechanism to its formal-kinetic features for two limiting cases. **Termination** via reaction (19). In this case, $w_{t,Ac} = 2k_{19}[CH_3COCH_2]^2$ and $w_{t,Me} = 0$, and the quasi-steady-state concentration of methyl radical is determined as follows:

$$[CH_{3}] = \frac{w_{M} + k_{1} [CH_{3}COCH_{2}][DMDO]}{k_{1} [CH_{3}COCH_{3}]}.$$
 (36)

The concentration of acetonyl radicals can easily be calculated from the condition $w_i = w_t$, then

$$[CH_3COCH_2] = [w_i/(2k_{19})]^{1/2}.$$
(37)

The rate w_i is determined by Eq. (27). Substitution of expressions (36) and (37) into Eq. (33) gives after simple rearrangements the expression for the rate of **1a** consumption:

$$w_{DMDO} = k^{(1.5)} [DMDO]^{3/2} + k^{(2)} [DMDO]^2 + k^{(2.5)} [DMDO]^{5/2},$$
(38)

in which the polynomial coefficients are combinations of the kinetic constants and acetone concentration. If the square-law termination via reaction (19) were the main pathway for radical decay, then the effective order with respect to [DMDO] would be within 1.5-2.5. As shown above, the consumption of dioxirane through the chain pathway is characterized by an order with respect to peroxide that is only somewhat higher than unity: $1 \le n \le 1.5$. Similarly, it is easy to show that termination via reaction (21) also does not correspond to the formal kinetics of the process under study.

Cross-termination via reaction (20). An assumption on the cross-decay of CH₃COCH₂⁺ and ⁺CH₃ seems to be most logical, taking into account the close reactivity of the carbon-centered radicals in the recombination/ disproportionation reaction. The radicals that cause 1a chain decomposition should be present in comparable quasi-steady-state concentrations. In the case of crosstermination, $w_{t,Ac} = w_{t,Me} = k_{20}[CH_3][CH_3COCH_2]$. The condition for the equality of the rates of initiation and termination should be the following:

$$[CH_{3}] = w_{i} / (k_{20} [CH_{3}COCH_{2}]).$$
(39)

Substitute expression (39) into Eq. (34) and take into account that $w_{Ac} = k_{Ac}[DMDO]$, $w_i = k_i[DMDO]$, then

$$k_{Ac}[DMDO] - k_{10}[CH_3COCH_2][DMDO] + + [k_1k_{16}[CH_3COCH_3]/(k_{20}[CH_3COCH_2])][DMDO] - - k_1[DMDO] = 0.$$
(40)

It is easily seen that the concentration of dioxirane in Eq. (40) cancels completely. Hence, the quasi-steadystate concentration of acetonyl radical, which can be calculated from this square equation, is independent of [DMDO]. As can be seen in Eq. (39), $[CH_3]$ is proportional to the concentration of dioxirane. Then Eq. (33) is rearranged into

$$w_{\rm DMDO} = k^{(1)} [\rm DMDO] + k^{(2)} [\rm DMDO]^2,$$
 (41)

where $k^{(1)}$ and $k^{(2)}$ are the complex combinations of the kinetic constants and [CH₃COCH₃]. The first term in

Eq. (41) characterizes the consumption of DMDO due to the reaction with acetonyl radical, $k^{(1)} = k_{10}[CH_3COCH_2]_{stat}$, and the quadratic term describes the contribution of reaction (13) to the overall rate w_{DMDO} .

Equation (41) agrees with the kinetic features found for the radical-chain decomposition of la when the first member of the sum contributes the most to w_{DMDO}. This condition is actually fulfilled, as the main product, acetol acetate, forms in the reaction of CH3COCH2. with 1a (see Table 1). The fact that the kinetics of the reaction is satisfactorily described by a first-order equation and the initial rate of the chain reaction (w_0) is proportional to [DMDO]₀ (see Table 3) reflects the domination of the first member in Eq. (41). The dependence of k_{ch} on the concentration of dioxirane and the linear correlation between $w_0/(DMDO)_0$ and $(DMDO)_0$ indicate the presence of the channel of la consumption, which is described by an equation of higher order. The change in the effective reaction order with respect to dioxirane within the limits from 1 to 1.5 also agrees with the above conclusions.

The differential equation (41) $(w_{DMDO} = d[DMDO]/dt)$ is easily reduced to the integral expression²⁰:

$$\ln \frac{(k^{(1)} + k^{(2)} [DMDO]) [DMDO]_0}{(k^{(1)} + k^{(2)} [DMDO]_0) [DMDO]} = k^{(1)}t.$$
 (42)

The constants $k^{(1)}$ and $k^{(2)}$ calculated from this equation are listed in Table 3. Let us evaluate the rate constant of the key reaction of the **1a** radical-chain decomposition under the assumption that the nature of the alkyl radical slightly affects the rate of the induced homolysis of the O-O bond, *i.e.*, $k_{10} \approx k_{13}$. It is obvious that

$$\frac{k^{(1)}k^{(2)}}{k^{(1)}k^{(1)}[CH_3][CH_3COCH_2]/[DMDO]} = \frac{k^2}{10} \frac{k$$

Since $w_t = w_i = 2\xi w_{DMDO} = 2\xi k_{eff} [DMDO]$, Eq. (43) is rearranged into the form

$$k_{10} = [k^{(1)}k^{(2)}k_{20}/(2\xi k_{\rm eff})]^{1/2}.$$
(44)

The recombination of alkyl radicals is determined by the mutual diffusion of the reactants and is in fact independent of the temperature; therefore, we can take $k_{20} = 5 \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. Substituting the $k^{(1)}$, $k^{(2)}$, ξ values (see Table 2 and 3) and $k_{\text{eff}} = 3.8 \cdot 10^{-5} \text{ s}^{-1}$ (calculated from the temperature dependence, see Fig. 2), we obtain $k_{10} = 1.6 \cdot 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$. The k_{10} value is in good agreement with the rate constants of the reactions of alkyl radicals with DMDO.13,20,24 It was suggested¹⁹ that the rate constant k(R' + DMDO) is close to the diffusion limit. This does not represent explicitly the facts because dioxirane, due to its reactivity $(k_{10} \approx k_{17})$ and the ratio between the concentrations $[DMDO]_0 >> [O_2]$, would trap all alkyl radicals even in the presence of O₂, resulting in the chain decomposition of 1a under any experimental conditions. A strong inhibiting effect of dioxygen indicates that $w_{17} >> w_{10}$ in the whole range of concentrations until its complete ($\leq 10^{-5}$ mol L⁻¹, *i.e.*, $\geq 99\%$) disappearance.

The kinetic analysis of the sequence of reactions (1)-(21) showed its qualitative correspondence to the products found and the kinetics of the radical-chain process under the assumption of chain termination according to reaction (20). Notably, the rate constant $k^{(1)}$ increases by the factor of ~2 when the [DMDO] increases fourfold (see Table 3), indicating the respective dependence of the quasi-steady-state concentration of the acetonyl radicals. The relation between [CH₃COCH₂]_{stat} and the dioxirane concentration points to the fact that a complex termination via reactions (19) and (20) is most probable. However, in this case, the expression for w_{DMDO} becomes too complicated for practical use.

The role of radical processes in the interaction between dioxirane and hydrocarbons. The experimental results demonstrate clearly the importance of homolytic processes in the system under study. A fraction of the radical mechanism becomes prevailing in reactions with aliphatic hydrocarbons. Note the conditions which can change the ratio between the two reaction channels.

- An increase in the temperature favors an increase in the contribution of the radical mechanism. According to the data of Table 2, the ξ value for isooctane increases from 57% (25 °C) to 73% (41 °C).

- The nature of the substrate oxidized. The higher the energy of homolytic dissociation of the C-H bond, the less the contribution of the radical reaction channel. The ξ value for tertiary hydrocarbons at 25 °C is 50-60% (see Table 2). *n*-Octane and cyclohexane possess stronger secondary C-H bonds; therefore, similar contributions of homolytic processes are observed for these compounds at a higher (41 °C) temperature.

The problem on the contribution of the molecular and radical channels in the reaction with a substrate of oxidation has repeatedly been discussed in the chemistry of oxidants of a peroxide nature. It is well known that the more pronounced the electrophilic properties of a peroxide (the affinity of an oxidant to an electron can likely be a measure of its activity) and the electron-donor properties of the oxidized compound, the lower the temperature, and the higher the polarity of a solvent, the more probable is the molecular process. A similar situation is apparently observed in the chemistry of dioxiranes. From a synthetic viewpoint, it is more advantageous to create conditions favoring the non-radical mechanism of the reaction: low temperatures, dioxirane with more pronounced oxidation ability (1b), and an oxidized compound with the activated C-H bonds capable of stabilizing effectively the positive charge on the C atom that arises because of a partial transfer of the electron density to oxirane. A conclusion on the molecular mechanism of the reaction has been drawn from the study¹⁷ of the processes under the above conditions. However, this cannot rule out the possibility of hydroxylation of saturated organic compounds via the radical pathway.

The problem of the mechanism of the reaction between dioxiranes and the C--H bond can be divided into two parts.

1. Do the radical processes occur during the interaction of dioxiranes with RH? By far, yes, and their contributions are determined by the chemical nature of the reactants, temperature, and solvent. A thesis on a "start-up of radical processes" 14.16 (*i.e.*, the radical processes are impossible without the necessary conditions: illumination, trace admixtures, *etc.*) seems to be rather incorrect. Sometimes, radical-chain processes determine the reaction pathway, for example, the oxidation of alicyclic hydrocarbons by dioxirane 1a at temperatures higher than room temperature. Obviously, situations are possible (see, for example, Ref. 17) in which the molecular channel prevails insomuch that even conditions favorable for the homolytic mechanism do not affect the occurrence of the oxidation process.

2. Does the hydroxylation of the C-H bond occur with the participation of free radicals? Our experimental data do not allow us to unambiguously answer this question. Examination of the experimental data gives evidence of the preference of the "oxenoid" mechanism but the homolytic pathway (primarily, latent-radical) cannot be ruled out.

One can assert with certainty that the interaction between dioxiranes and saturated organic compounds is a complicated process that involves the molecular and radical mechanisms as the limiting cases. Therefore, simplified concepts on the occurrence of only one of them are incorrect.

The work was financially supported by the Russian Federal Program "Government Support for the Integration of Higher Education and Basic Science for 1997-2000" under State contract No. 2.1-573.

References

- W. Adam, R. Curci, and J. O. Edwards, Acc. Chem. Res., 1989, 22, 205.
- 2. R. W. Murray, Chem. Rev., 1989, 89, 1187.
- 3. W. Adam and L. Hadjiarapoglou, Top. Curr. Chem., 1993, 164, 45.
- 4. R. Curci, A. Dinoi, and M. F. Rubino, Pure and Appl. Chem., 1995, 67, 811.
- 5. R. W. Murray and H. Gu, J. Org. Chem., 1995, 60, 5673.
- 6. R. W. Murray and H. Gu, J. Chem. Soc., Perkin Trans. 2, 1994, 451.
- R. W. Murray, R. Jeyaraman, and L. Mohan, J. Am. Chem. Soc., 1986, 108, 2470.
- R. Mello, M. Fiorentino, C. Fusco, and R. Curci, J. Am. Chem. Soc., 1989, 111, 6749.
- W. Adam, R. Curci, M. E. G. Nunez, and R. Mello, J. Am. Chem. Soc., 1991, 113, 7654.
- 10. M. Singh and R. W. Murray, J. Org. Chem., 1992, 57, 4263.
- F. Minisci, L. Zhao, F. Fontana, and A. Bravo, *Tetrahedron Lett.*, 1995, 36, 1697.

- F. Minisci, L. Zhao, F. Fontana, and A. Bravo, *Tetrahedron Lett.*, 1995, 36, 1895.
- A. Bravo, F. Fontana, G. Fronza, A. Mele, and F. Minisci, J. Chem. Soc., Chem. Commun., 1995, 1573.
- 14. R. Curci, A. Dinoi, C. Fusco, and M. A. Lillo, *Tetrahedron Lett.*, 1996, 37, 249.
- A. Dinoi, R. Curci, P. Carloni, E. Damiani, P. Stipa, and L. Greci, Eur. J. Org. Chem., 1998, 871.
- W. Adam, R. Curci, L. D'Accolti, A. Dinoi, C. Fusco, F. Gasparrini, R. Kluge, R. Paredes, M. Schulz, A. K. Smerz, L. Angela Veloza, S. Weinkotz, and R. Winde, *Chem. Eur. J.*, 1997, 3, 105.
- 17. P. A. Simakov, S.-Y. Choi, and M. Newcomb, *Tetrahedron Lett.*, 1998, **39**, 8187.
- G. Asensio, R. Mello, M. E. Gonzalez-Nunez, C. Boix, and J. Royo, *Tetrahedron Lett.*, 1997, 38, 2373.
- A. Bravo, F. Fontana, G. Fronza, F. Minisci, and L. Zhao, J. Org. Chem., 1998, 63, 254.
- D. V. Kazakov, N. N. Kabal'nova, S. L. Khursan, and V. V. Shereshovets, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 694 [*Russ. Chem. Bull.*, 1997, 46, 663 (Engl. Transl.)].
- 21. L. A. Hull and L. Budhai, Tetrahedron Lett., 1993, 34, 5039.
- S. A. Grabowski, D. V. Kazakov, N. N. Kabalnova, S. L. Khursan, and V. V. Shereshovets, *React. Kinet. Catal. Lett.*, 1997, 62, 179.
- S. A. Grabowski, N. N. Kabal'nova, S. L. Khursan, and V. V. Shereshovets, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1321 [*Russ. Chem. Bull.*, 1998, **47**, 1284 (Engl. Transl.)].
- 24. D. V. Kazakov, D. R. Khusnullina, N. N. Kabal'nova, S. L. Khursan, and V. V. Shereshovets, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1785 [*Russ. Chem. Bull.*, 1997, 46, 1690 (Engl. Transl.)].
- 25. D. R. Khusnullina, D. V. Kazakov, N. N. Kabal'nova, S. L. Khursan, and V. V. Shereshovets, *Kinet. Katal.*, 1998, **39**, 8 [*Kinet. Catal.*, 1998, **39** (Engl. Transl.)].
- R. W. Murray and R. Jeyaraman, J. Org. Chem., 1985, 50, 2847.
- 27. W. Adam, J. Bialas, and L. Hadjiarapoglou, Chem. Ber., 1991, 124, 2377.
- V. B. Kogan, V. M. Fridman, and V. V. Kafarov, *Spravochnik po rastvorimosti* [Handbook on Solubility], Izd-vo Akad. Nauk SSSR, Moscow, 1961, 1, book 1 (in Russian).
- M. Ferrer, M. Gibert, F. Sanchez-Baeza, and A. Messeguer, Tetrahedron Lett., 1996, 37, 3585.
- D. Cremer, E. Kraka, and P. G. Szalay, Chem. Phys. Lett., 1998, 292, 97.
- 31. P. Neta, R. E. Huie, and A. R. Ross, J. Phys. Chem. Ref. Data, 1990, 19, 413.
- 32. E. T. Denisov and V. V. Azatyan, Ingibirovanie tsepnykh reaktsii [The Inhibiton of Chain Reactions], Izd-vo IKhFCh RAN, Chernogolovka, 1997 (in Russian).
- 33. G. V. Shustov and A. Rauk, J. Org. Chem., 1998, 63, 5413.
- 34. G. A. Russell, J. Am. Chem. Soc., 1957, 79, 3871.
- 35. J. A. Howard, Advances in Free Radical Chemistry, 1972, 4, 49.
- 36. D. G. Hendry, T. Mill, L. Piszkiewicz, J. A. Howard, and H. K. Eigenmann, J. Phys. Chem. Ref. Data, 1974, 3, 937.
- 37. H. Paul, R. D. Small, and J. C. Scaiano, J. Am. Chem. Soc., 1978, 100, 4520.

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