Kinetics and mechanism of the reaction of dimethyldioxirane with cumene

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The reaction of dimethyldioxirane with cumene $(22-52 \,^{\circ}\text{C})$ follows a chain-radical mechanism. The kinetic regularities of this reaction were studied by the chemiluminescence and kinetic UV spectrophotometry methods by monitoring the consumption of dioxirane. The process is inhibited by oxygen. In the absence of O₂, the process is accelerated due to the decomposition of dimethyldioxirane induced by alkyl radicals. In this case, the reaction occurs according to a complicated kinetic law including the first and second orders with respect to dioxirane. Based on the kinetics and reaction products, the scheme of the process was proposed.

Key words: kinetics, mechanism, dioxiranes, free radicals.

Selective oxidation of organic compounds to the corresponding hydroxy- and oxo-derivatives is of great theoretical and practical interest. Dioxiranes, which combine high selectivity and mild oxidation conditions, are very promising oxidants for organic compounds.^{1,2} The majority of studies on the chemistry of dioxiranes are devoted to revealing their synthetic possibilities. The study of the mechanisms of oxidation processes involving dioxiranes is also an urgent problem. Two mechanisms of the reactions of dioxiranes with saturated organic compounds are discussed: insertion at the C-H bond and the radical mechanism³



is the high stereospecificity of the oxidation process.³⁻⁵ For example, the oxidation of R-(-)-2-phenylbutane by methyl(trifluoromethyl)dioxirane occurs with the complete retention of the configuration.⁵ The value of the constant of the reaction series $\rho = -2.76$ for the oxidation of *para*-substituted cumenes by dimethyldioxirane⁶ agrees well with the insertion mechanism. The primary isotope effect $(k_{\rm H}/k_{\rm D} = 4.97$ for the oxidation of cyclododecane-d₂₄ and $k_{\rm H}/k_{\rm D} = 2$ for cyclohexane-d₁₂^{3,4}) and the high selectivity (the ratio of the rate constants of the reactions of dimethyldioxirane with toluene, ethylbenzene, and cumene calculated per benzyl C—H bond is equal to 1 : 24 : 91)³ are also evidence for the nonradical character of the process. The inhibitory effect of *para*-benzoquinone and 2,2,6,6-tetramethylpiperidineoxyl on the oxidation of hydrocarbons by dimethyldioxirane⁹ agrees with the radical scheme.⁷⁻⁹



Another argument in favor of the radical mechanism is the effect of oxygen on the rate and composition of the oxidation products.⁷⁻⁹

Evidently, the mechanism of the reaction of dioxirane with the C—H bond depends on a number of factors (the nature of reagents, solvent, and temperature). The possibility that the reaction proceeds simultaneously via several pathways with different degree of charge separation in the transition states cannot be ruled out.⁴

Data on the reaction kinetics give very useful information on the mechanism of the process. Therefore, in the present work, the kinetic regularities of the reaction of dimethyldioxirane (DMDO) with cumene (CumH) are studied in detail along with the composition of the products, and the scheme of the process is suggested on the basis of this study.

Experimental

Dimethyldioxirane was synthesized, identified, and analyzed as described previously.⁸ Isopropylbenzene (cumene, CumH) was purified by a known procedure.¹⁰ The reaction products were analyzed on a Finnigan GLC mass spectrometer and by GLC on a Shimadzu chromatograph (PEG-20M. l = 25 m, 50-180 °C). The concentrations of DMDO and CumH were measured within $(1.2-5.7)\cdot 10^{-2}$ mol L⁻¹ and 0.45–1.8 mol L⁻¹, respectively. The reaction kinetics was studied spectrophotometrically by the consumption of DMDO at $\lambda = 335 \text{ nm}$ ($\varepsilon = 10 \text{ Lmol}^{-1} \text{ cm}^{-1}$) on a Specord M-40 instrument. A solution (2–2.5 mL) of DMDO in acetone was placed in a quartz cell (the optical path was 1 cm), and argon was bubbled through the solution for ~2.5 min. The cell was placed in a

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 4, pp. 694-702, April, 1997.

1066-5285/97/4604-0663 \$18.00 © 1997 Plenum Publishing Corporation

chamber of the spectrophotometer and thermostated at $42 \,^{\circ}$ C (the concentration of DMDO remained almost unchanged during thermostating). The necessary amount of CumH was rapidly added by a syringe, with a negligible change in the temperature. The cell was tightly closed, and the consumption of DMDO was monitored. Some experiments were performed with continuous bubbling of oxygen.

Chemiluminescence (CL) was detected on an installation with an FEU-140 photomultiplier. For detection of CL, cumene (1 mL) or a solution of cumene in CCl₄ and a solution (0.8 mL) of DMDO (0.06 mol L^{-1}) in acetone were placed in a reactor with a stirrer and a bubbler. The temperature was varied in the range from 22 to 52 °C.

Results and Discussion

Reaction products. The main products of the reaction of CumH and DMDO at 42 °C with continuous bubbling of oxygen are 2-phenylpropan-2-ol (CumOH) and acetophenone (PhC(O)Me), in yields of 0.6 and 0.34 moles per mole of DMDO (Table 1). The ratio Δ [CumOH]/ Δ [PhC(O)Me] = 1.78 is close to that calculated using the data from Ref. 11 for the initiated oxidation of cumene (1.45) at [CumH] = 1 mol L⁻¹ and 42 °C.

In an inert atmosphere (the oxygen that is initially present in the system is either chemically bound or removed by bubbling of Ar), the yields of CumOH and PhC(O)Me per converted DMDO are lower (see Table 1). In addition, cumyl acetate, α -methylstyrene, α -methylstyrene oxide, and *tert*-butylbenzene are observed in the products. The formation of these compounds can be explained only by radical processes. Thus, even a simple study of the reaction products makes it possible to conclude that the reaction occurs *via* the radical route.

Reaction kinetics in an oxygen atmosphere. Under these conditions, the reaction kinetics were studied by the CL method at $[CumH]_0 > [DMDO]_0$ ($[CumH]_0$ and $[DMDO]_0$ are the initial concentrations of cumene and dimethyldioxirane, respectively) and at $[O_2]_0 = (5 6) \cdot 10^{-3}$ mol L⁻¹. We have previously shown that the reaction of DMDO with cumene is accompanied by CL in the visible spectral region.¹² It is important that CL is observed only in the presence of O_2 . When the O_2 supply is stopped, the luminescence decays, which is a convincing argument that the luminescence is caused by the recombination of peroxyl radicals. The typical kinetic curves of the luminescence decay presented in

Table 1. Products of the reaction of dimethyldioxirane with cumene

T/°℃	[DMD0]	[CumH]	[CumOH] · 10 ²	{PhC(O)Me}-10 ²
			/mol L ⁻¹	
36	0 04	1.0	0.83	0.38
51	0.04	10	0 85	0.35
42*	0.04	10	2.43	1.36

The experiment was carried out with continuous bubbling of oxygen

Fig. 1 can be linearized $(r \ge 0.99)$ in the coordinates of first-order equation. Rate constants of a pseudo-first order k_{eff} were calculated from the kinetic curves of the CL decay:

[CumH]/mol L ⁻¹	0.45	2.0	3.0	4.5
$k_{\rm eff} \cdot 10^3 / {\rm s}^{-1}$	0.84 ± 0.08	4.6±0.4	6.3±0.6	8.7±0.7
$([DMDO]_0 = 2.8 \cdot$	10 ⁻² mol L ⁻¹ ,	CCl ₄ as so	lvent, 42 °	C).

The temperature dependence $k_{eff}([CumH] = 4 \text{ mol } L^{-1})$

T/K	295	303	310	315	317	325
$k_{et\bar{t}} \cdot 10^3/s^{-1}$	1.11	2.86	4.06	7.72	5.32	8.0

is described by the equation $\log k_{\text{eff}} = 6.4 - (12.5 \pm 2.2)/\theta$ $\theta = 2.303 \cdot RT \text{ kcal mol}^{-1}$.

Reaction kinetics in an inert atmosphere. The reaction kinetics were studied spectrophotometrically by measuring the consumption of dimethyldioxirane over time at $[CumH]_0 > [DMDO]_0$. The kinetic curves of consumption of DMDO have an S-like character. The initial regions of the kinetic curves in the induction period can be described by a first-order equation (Fig. 2). The rate constants agree satisfactorily with the values obtained in experiments in an atmosphere of O₂. The existence of the induction period is likely related to the inhibiting action of the O_2 that is present in the solution. This is indicated by a decrease in the induction period when argon is bubbled through the system. An increase in the concentration of cumene also results in a decrease in the induction period due to the more efficient binding of O_2 (see Fig. 2). Continuously bubbling O₂ through the system constantly inhibits the system and, as a consequence, autoacceleration of the process does not occur. Unfortunately, in an atmosphere of O_2 ,



Fig. 1. Time dependence of the intensity of CL in the CumH-DMDO system (42 °C, $[CumH]_0 = 2.0 \text{ mol } L^{-1}$, $[DMDO]_0 = 0.028 \text{ mol } L^{-1}$, solvent CCl₄).



Fig. 2. Typical kinetic curves of consumption of DMDO (42 °C, acetone) (1-4) and their anamorphoses (2a, 2b, 3a, 4a). 1, [CumH]₀ = 0; 2, oxygen was preliminarily bubbled through the reaction mixture, [CumH]₀ = 0.75 mol L^{-1} ; 3 and 4, argon was preliminarily bubbled through the reaction mixture, [CumH]₀ = 0.75 and 1.5 mol L^{-1} , respectively.

the reaction kinetics cannot be studied spectrophotometrically, because the spectra of DMDO and oxidation products are superposed. As the reaction conversion increases, the concentration of O_2 decreases due to its chemical binding, and the process is sharply accelerated. Under these conditions, the kinetic order with respect to dioxirane increases as the reaction develops. The kinetic

Table 2. Effective one-and-half-order constants $(k/L^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1})$ of consumption of DMDO in cumene (42 °C, acetone)

[DMDO]* · 10 ² /mol L ⁻¹	k · 10 ³	[CumH]** /mol L ⁻¹	k · 10 ³
1.2	7.2	0.45	23.7
2.2	17.1	0.75	21.3
3.0	16.6	1.0	25.5
4.2	27.3	1.3	32.8
5.1	28.3	1.5	38.8
5.7	- 39.4	1.8	41.8

* $[CimH] = 1 \mod L^{-1}$. ** $[DMDO] = 0.04 \mod L^{-1}$.

curves are described with reasonable correlation coefficients by equations of either one and half or second orders. The effective rate constants that formally describe the kinetics of the consumption of DMSO under different conditions are presented in Table 2.

According to Table 2, k increases as the concentrations of CumH and DMDO increase. The dependence of k on the concentration of dioxirane testifies that the time order of the reaction with respect to dioxirane determined by the integral method differs from the true order. This situation is characteristic of complicated processes, in particular, of the case when the products are involved in the reaction.¹³ In fact, since both α -methylstyrene and its oxide were observed in the products, it can be supposed that the increase in the rate constant is caused by the epoxidation of styrene by dimethyldioxirane. It is known¹⁴ that dioxirane efficiently epoxidizes alkenes. It has been determined by the spectrophotometric method that the second-order rate constant of the reaction of DMDO with α -methylstyrene is equal to 2.0±0.4 L mol⁻¹ s⁻¹ (25 °C, acetone).

The experimental results obtained testify convincingly that the reaction of DMDO with cumene involves free-radicals:

a. The effect of O_2 on the kinetics of the process. The substantial retardation of the reaction in the presence of O_2 is associated with the diffusion-controlled reaction of the latter with alkyl radicals. Since under the conditions studied the ROO⁺ radicals cannot induce the decomposition of DMDO, the reaction $R^+ + O_2$ is in fact the stage of termination at the inhibitor (O_2). The shape of the kinetic curves and the dependence of the reaction rate on the concentration of O_2 are characteristic of chain-radical inhibited processes.

b. The formation of such reaction products as acetophenone, α -methylstyrene, and *tert*-butylbenzene is possible for the radical process.

c. The ratio of the concentrations of the main reaction products (2-phenylpropan-2-ol and acetophenone) is characteristic of radical processes, in which the cumyloxyl radical is generated to be either decomposed or to eliminate the H atom.

d. The detection of CL in the visible spectral region is evidence for the existence of radical intermediates. The presence of oxygen in solution is necessary for the appearance of luminescence. This suggests that peroxyl radicals are responsible for the CL observed.

Mechanism of the process. The combined experimental (kinetics, reaction products) and published data suggest the following mechanism of the reaction.

Generation of free radicals. Although free radicals appear only in reaction (+1), the reactions leading to the primary products and carbon-centered radicals were also included in this group of reactions.

The first stage of the process resulting in the generation of free radicals is homolysis of the O-O bond of dioxirane. The bond strength in acyclic peroxides is





equal to 37-38 kcal mol⁻¹, ¹⁵ and the strain energy of the three-membered cycle is '-26 kcal mol-1,16 therefore, the dissociation energy of the O-O bond in dioxirane is equal to 11-12 kcal mol⁻¹. The quantumchemical estimations give 15 kcal mol^{-1,1} The biradical formed is transformed into the initial dioxirane via reaction (-1) and is decomposed (reactions (2a), (2b)) or attacks the C-H bond of the solvent molecule (reactions (3a), (3b)) or cumene ((4a), (4b)). Hereinafter, the decomposition of the biradical and elimination of the H atom of the acetone molecule are neglected due to the rather high concentration of cumene and the high strength of the C-H bond in acetone. In fact, the initial rate of the decomposition of DMDO in the presence of cumene (in an atmosphere of O_2) is more than an order of magnitude higher than that in the absence of cumene, which indicates that reactions (4a) and (4b) predominate. The following reactions are possible for the hydroxyalkoxyl radical formed:

destruction:

$$HO = -6.3 \text{ kcal mol}^{-1})$$
(5a)
(5a)
(5a)
(5a)
(5b)
(5b)
(5b)

or elimination of the hydrogen atom:

$$\bigvee_{0}^{OH} + = 0 \longrightarrow \bigvee_{OH}^{OH} + CH_2C(O)Me$$
, (6)

$$\bigvee_{O}^{OH} + CumH \longrightarrow \bigvee_{OH}^{OH} + Cum^{-1}, \qquad (7)$$
$$(\Delta H^{0} = -21.5 \text{ kcal mol}^{-1})$$

$$HO' + H_2O + CH_2C(O)Me .$$
(8)

$$HO' + CumH \longrightarrow H_2O + Cum'.$$
(9)

The tetrahedral intermediate formed in reactions (3b), (4b), (6), and (7) is decomposed to acetone and the hydroxy-derivative:

$$\bigvee_{OR}^{OH} \longrightarrow PO + ROH.$$
(10)

where R = H, $CH_2C(O)Me$, Cum.

The heat effects of the reactions were calculated for the standard state (ideal gas, 1 atm, 298 K) from the enthalpies of formation of the molecules and radicals presented in Table 3.

Since acetic acid was not found in the oxidation products and stage (5b) is strongly exothermic, reactions (5a) and (5b) can be neglected. Therefore, the main

 Table 3. Enthalpies of formation of molecules and radicals (ideal gas, 1 atm, 298 K)



^a See Ref. 17. ^b Calculated by the equation $\Delta_f H^0(RO^+) = \Delta_f H^0(ROH) + 52.0.^{18}$ ^c Calculated by the Benson method.¹⁶ ^d See Ref. 19.

route of transformation of the hydroxyalkoxyl radical is reaction (7). Thus, for the generation of free radicals, the sequence of stages (1), (4a), (7), and (10) is most probable, and it can be written as the overall reaction

$$\swarrow_0^0 + 2CumH \longrightarrow 2Cum + = 0 + H_2^0$$

Intracage recombination (4b) results in the formation of 2-phenylpropan-2-ol. Most likely, the contribution of this channel is relatively small, since the ratio of the concentrations [CumOH]/[PhC(O)Me] is close to that obtained for the competition between elimination of the H atom and decomposition of the cumyloxyl radical.¹¹ In our case, these reactions are also the main reactions of the formation of the compounds indicated.

Mechanism of the reaction in the presence of oxygen. A fairly low reaction rate is a characteristic feature of the process in the presence of oxygen. In particular, the induction periods observed in the kinetic curves (see Fig. 2) are caused by chemical binding of the initially present O_2 . The cumyl radicals formed at the initiation stage are rapidly transformed into cumylperoxyl radicals in an atmosphere of O_2 (the rate constant of this process $k > 10^9$ L mol⁻¹ s⁻¹):²⁰

$$Cum' + O_2 \longrightarrow CumOO'. \tag{11}$$

Since the decrease in the concentration of DMDO in the induction period (see Fig. 2) is equal to $\sim 10^{-3}$ mol L⁻¹ and is comparable to the concentration of dissolved O₂, it can be supposed that the peroxy radicals do not react with DMDO and decay predominantly in a recombination reaction, whose mechanism has been previously described in detail.^{21,22}

Cumene tetraoxide is irreversibly decomposed to form cumyl oxide radicals in the solvent cage. These radicals can recombine to give dicumene peroxide or diffuse from the cage.

CumOOOOCum
$$\longrightarrow$$
 CumO' + O₂ + 'OCum \longrightarrow
CumOOCum + O₂ (13a)
 2 CumO' + O₂ (13b)

The cumyl oxide radical can undergo β -decomposition to form acetophenone and a methyl radical or participate in chain transfer:

$$CumO \longrightarrow Ph \longrightarrow O + Me$$
 (14)

The cumyl oxide radical can also attack the primary C-H bond of cumene:²²

In an oxygen atmosphere, the alkyl radicals (Me⁺, Cum⁺, Cum⁺) are rapidly oxidized to the peroxyl radicals, which continue the oxidation chain or (in the case of the MeOO⁺ and Cum⁺OO⁺ radicals) decay in the cross reaction of chain termination. In the latter reaction, the triplet-excited aldehyde is formed,²² whose emission results in the CL observed:

$$Cum''(Me') + O_2 \longrightarrow Cum'OO'(MeOO'),$$
 (16)

$$ROO' + CumH \longrightarrow ROOH + Cum',$$
 (17)

Cum'00' + Cum00' ----- Cum0H + O_2 +

The main products of the reaction of DMDO with cumene in an atmosphere of O_2 are 2-phenylpropanol-2 and acetophenone, which are formed, as follows from the scheme, mainly by reactions (14) and (15). The overall yield of acetophenone and 2-phenylpropanol-2, calculated per DMDO consumed, is equal to 94% (see Table 1). Thus, the sequence of reactions (1), (4a), (7), and (10) is predominant in the consumption of DMDO in an atmosphere of O_2 .

In terms of the scheme, the intensity of CL (1) is proportional to the rate of reaction (18):

$$I = \varphi w_{18} = \varphi k_{18} [CumOO^{+}] [Cum'OO^{+}].$$
(1)

The kinetic consequences of the mechanism of decay of the cumylperoxyl radicals presented above have been analyzed in detail previously.²² When the concentrations of cumene are high, chain termination reactions (13a) and (18) occur at comparable rates, while the contribution of the MeOO⁻ radicals to the overall decay of the radicals is minimum. Under steady-state conditions, the initiation rate is equal to the sum of the rates of the chain termination reactions

$$w_1 = 2ek_{eff}[DMDO] = w_{13a} + w_{18} =$$

= $(k_{13a} + 2\delta k_{18})[CumOO^+]^2$. (II)

The combination of Eqs. (1) and (11) results in the equation

$$I = 2e\varphi k_{\text{eff}}(1-\zeta) \{\text{DMDO}\},\tag{III}$$

where e is the probability of escape of the radicals from the solvent cage (reaction (4)), δ is the ratio of the rate constants of chain termination by the CumOO⁺ and 668

Cum'OO' radicals via reaction (17);²² $\zeta = k_{13a}/(k_{13a} + 2\delta k_{13})$.

Using the quasi-steady-state principle with respect to the biradical intermediate, we obtain $I_0/I = \exp(k_{+1}k_4[\operatorname{CumH}] \cdot t/(k_{-1} + k_4[\operatorname{CumH}]))$, where I_0 is the intensity of luminescence at the initial moment. It has been experimentally determined that the kinetics of CL decay can be described by the equation $I_0/I = \exp(k_{\text{eff}} \cdot t)$, from where it follows

$$k_{\rm eff} = \frac{k_{+1} \cdot k_4 [\rm CumH]}{k_{-1} + k_4 [\rm CumH]}.$$
 (IV)

Under the condition $k_{-1} > k_4$ [CumH], the effective rate constant k_{eff} is proportional to the concentration of cumene, which is observed in the experiment (see above).

Mechanism of the reaction in the absence of oxygen. Bubbling argon through the reaction mixture or chemical binding of oxygen result in sharp enhancement of the reaction (see Fig. 2). In the absence of O_2 , the mechanism of the process can be presented by the following sequence of stages:

chain generation (similar to that presented above);

chain propagation involving the decomposition of DMDO induced by the alkyl radicals:

$$\bigvee_{0}^{0} + Cum^{2} \xrightarrow{0}_{0}^{0} Cum$$

$$(M^{0} = -52.9 \text{ kcal mol}^{-1})$$
(19)

The intermediate formed can decompose via two pathways or eliminate the H atom from the cumene molecule.

$$CumO \rightarrow Me^{-1}$$

$$(20a)$$

$$(20a)$$

$$\bigvee_{0}^{\text{OCum}} \xrightarrow{} 0^{+} \text{CumO}^{-} (20b)$$

$$(\Delta H^{0} = +0.4 \text{ kcal mol}^{-1})$$

$$+ CumH \rightarrow Cum \rightarrow Cum (20c)$$

The Me radical reacts similarly.

$$\bigvee_{0}^{0} + Me^{2} \longrightarrow_{0}^{0Me}$$

$$(\Delta H^{2} = -70.2 \text{ kcal mol}^{-1})$$
(21)



$$(\Delta H^{0} = -5.9 \text{ kcal mol}^{-1})$$

$$(\Delta H^{0} = -5.9 \text{ kcal mol}^{-1})$$

$$(\Delta H^{0} = +9.4 \text{ kcal mol}^{-1})$$

$$(\Delta H^{0} = +9.4 \text{ kcal mol}^{-1})$$

$$(\Delta H^{0} = +9.4 \text{ kcal mol}^{-1})$$

$$(22b)$$

$$(\Delta H^{0} = +9.4 \text{ kcal mol}^{-1})$$

$$(22c)$$

The alkoxy radicals formed in reactions (20b) and (22b) regenerate alkyl radicals according to reactions (14), (15a), and (23);

$$MeO' + CumH \longrightarrow MeOH + Cum^{-}$$
, (23)

chain termination: since two carbon-centered radicals are present in the system, chain termination can occur via three channels (reactions (24)-(26)).

Cum' + Cum'
$$(24a)$$

Cum' + Cum' Ph
CumH + CumH (24b)

+ Me'
$$\rightarrow$$
 CH₄ + Ph \rightarrow CH₂ (25b)

Let us consider the kinetic consequences of this mechanism. The rate of decomposition of DMDO is determined by the equation

Cum

Me

$$-\frac{d[DMDO]}{dt} = k_{eff}[DMDO] + k_{19}[Cum'][DMDO] + k_{21}[Me'][DMDO], \quad (V)$$

where k_{eff} is the effective constant of the decomposition of dioxirane in an atmosphere of O₂ (see Eq. (IV)).

Using the quasi-steady-state approach for the concentrations of Cum⁺ and Me⁺, we obtain

$$\frac{d[\text{Cum}]}{dt} = 2ek_{\text{eff}}[\text{DMDO}] - \alpha \cdot k_{19}[\text{Cum}^{+}][\text{DMDO}] + (1 - \beta)k_{21}[\text{Me}][\text{DMDO}] - w_{t,\text{Cum}} = 0, \quad (\text{VI})$$

$$\frac{d[Me]}{dt} = \alpha \cdot k_{19}[Cum^{+}][DMDO] - (1-\beta)k_{21}[Me^{+}][DMDO] - w_{1Me} = 0, \qquad (V11)$$

where e is the probability of escape of the radicals from the solvent cage (reaction (4)): α and β are the probabilities of formation of the Me^{\cdot} radical from the Me₂C(OCum)O^{\cdot} (reactions (20a-c), (14), and (15a)) and Me₂C(OMe)O^{\cdot} intermediates (reactions (22a-c) and (23)), respectively.

The kinetic order with respect to [DMDO] is determined by the predominant stage of chain termination.

a. Cum' + Cum' termination. In this case, $w_{t,Me} = 0$, $w_{t,Cum} = 2k_{24}[Cum']^2$, which results in a decrease in the initiation and termination rates in Eq. (VI) and the simple correlations

 $\alpha k_{19}[\text{Cum}^+] = (1 - \beta)k_{21}[\text{Me}^+], \qquad (\text{VIII})$

$$k_{24}[\text{Cum}^*]^2 = ek_{\text{eff}}[\text{DMDO}]. \tag{1X}$$

It follows from Eqs. (VIII) and (IX) that the concentrations of the alkyl radicals are proportional to $[DMDO]^{1/2}$. In this case, Eq. (V) takes the form

$$-\frac{d[DMDO]}{dt} = k^{(1)}[DMDO] + k^{(1.5)}[DMDO]^{3/2},$$
 (X)

where $k^{(1)}$ and $k^{(1.5)}$ are the rate constants describing the overall effect of the decomposition of DMDO by the corresponding kinetic orders.

b. Cum' + Me' termination. Here $w_{t,Me} = w_{t,Cum} = k_{25}[Cum'][Me'] = ek_{eff}[DMDO]$. Cross termination is possible when the concentration of methyl radicals is rather high. Therefore, the probability β must be close to unity, and Eqs. (VI) and (VII) can be written in the form

$$ek_{\text{eff}}[\text{DMDO}] = \alpha k_{19}[\text{Cum}^+][\text{DMDO}] = k_{25}[\text{Cum}^+][\text{Me}^+]. \quad (XI)$$

Thus, in the case of cross chain termination, the concentration [Cum⁻] is independent of [DMDO], [Me⁻] is proportional to the concentration of dioxirane, and Eq. (V) takes the form

$$-\frac{d[DMDO]}{dt} = k^{(1)}[DMDO] + k^{(2)}[DMDO]^2, \qquad (XII)$$

where $k^{(2)}$ is the effective second-order constant.

c. Me⁺ + Me⁺ termination. In this case, $w_{t,Cum} = 0$, $w_{t,Me} = 2k_{26}[Me^+]^2$. A necessary condition for squared termination at methyl radicals is the predominant formation of Me⁺ in the induced decomposition of DMDO (stages (19)-(23)), *i.e.*, $\alpha = \beta = 1$. From this it follows that

 $2ek_{eff}[DMDO] = k_{19}[Cum^+][DMDO] = 2k_{26}[Me^+]^2$. (XIII)

The concentration of cumene radicals is independent of the concentration of dioxirane, and $\{Me^+\}$ is proportional to $[DMDO]^{1/2}$. This results in an equation of consumption of dioxirane that is similar to Eq. (X).

Thus, the evidence for a complicated kinetic law describing the decomposition of DMDO that was obtained in this work and observed previously^{7,8,23} can be explained by the analysis of the scheme of the process. When chain termination occurs *via* several reactions, the

kinetic description is more complicated than that presented by Eqs. (X) and (XII).

The choice between different versions of the mechanism suggested can be based on the analysis of the reaction products. The experimental results suggest that cross decay of the alkyl radicals is more probable:

- the formation of the main products (cumyl and methyl acetates) is accompanied by the parallel formation of the Me⁺ radical;

- the ratio of the concentrations [CumOH]/ [PhC(O)Me] testifies that the cumyloxyl radical participates in the process (see above). However, the yield of these products is considerably lower than that in the reaction in an atmosphere of O_2 . This indicates that the contribution of the reactions involving methyl radicals is significant;

- the absence of methanol in the reaction products is evidence for the negligible contribution of reactions (22b), (22c), and (23) and for the high probability of regeneration of the methyl radical in the sequence of reactions (21)-(23), *i.e.*, $\beta = 1$;

- dicumyl was not detected in the reaction products, which decreases the probability of reaction (24);

- a high probability of cross chain termination is directly indicated by the observation of *tert*-butylbenzene, α -methylstyrene, and the product of its epoxidation:

$$\swarrow_{0}^{0} + \stackrel{\mathsf{Ph}}{\longrightarrow} CH_{2} \longrightarrow 0 + \stackrel{\mathsf{Ph}}{\longrightarrow} \bigcup_{0}^{CH_{2}} (27)$$

The thermochemical calculations of the heat effects of the reactions agree with the mechanism proposed. In fact, reaction (21) is more exothermic than reaction (19), which indicates that the methyl radical is more reactive. The decomposition of the alkoxyl intermediates formed in these reactions is more probable for directions (20a) and (22a). Reaction (22b) is endothermic by ~10 kcal mol⁻¹ and likely does not occur under our experimental conditions, which results in a high probability of β -regeneration of the Me⁺ radicals. By contrast, stage (20b) is thermally neutral and can occur at a high rate.

Thus, in an inert atmosphere, the reaction of cumene and dimethyldioxirane is described by the sequence of reactions (1), (4), (7), (10), (14), (15a), (19)-(21), (22a), (25), and (27).

Using the quasi-steady-state principle over all radical intermediates and α -methylstyrene (this is justified due to the high rate constant of epoxidation) and assuming that $\beta = 1$, we can obtain the following equation for the rate of consumption of DMDO:

$$-\frac{d[DMDO]}{dt} = \frac{(1 + e\tau + e / a) \cdot k_{+1}k_{4}[CumH]}{k_{-1} + k_{4}[CumH]} [DMDO] + \frac{ak_{1}gk_{21}}{k_{22} + k_{22}} [DMDO]^{2}, \qquad (XIV)$$

where $\tau = k_{25b}/(k_{25a} + k_{25b})$ is the probability of the disproportionation stage in the overall decay of the radicals; $\alpha = \varepsilon_1 + \varepsilon_{2\gamma}$, where $\varepsilon_1 = k_{20a}/(k_{20a} + k_{20b} + k_{20c}[\text{CumH}])$, $\varepsilon_2 = k_{20b}/(k_{20a} + k_{20b} + k_{20c}[\text{CumH}])$, and $\gamma = k_{14}/(k_{14} + k_{15a}[\text{CumH}])$.

According to Eq. (XIV), the observed reaction order with respect to [DMDO] should be between 1 and 2. In this connection, a satisfactory approximation of the reaction kinetics by a law of 3/2 (see Table 2) is quite probable. Equation (XIV) describes satisfactorily both the kinetic regularities at the initial stage of the process and the whole kinetic curve of the decomposition of DMDO under the condition of excess CumH. The values of the initial rates w_0 are presented in Table 4, from which it can be seen that at [CumH] = 1.0 mol L⁻¹ the $w_0/[DMDO]_0$ ratio depends linearly on [DMDO]_0 (Fig. 3):

$$w_{\rm th} / [\rm DMDO]_0 = (1.4 \pm 0.9) \cdot 10^{-3} + (0.30 \pm 0.02) [\rm DMDO]_0.$$
 (XV)

Thus, in an inert atmosphere, the main contribution to the decomposition of DMDO is made by the induced decomposition of the latter by the Me⁺ radicals. When [DMDO] = $5 \cdot 10^{-2}$ mol L⁻¹, the fraction of the channel of second order decomposition is equal to ~90%. According to the data in Table 4, the reaction rate increases as the concentration of cumene increases. However, the experimental results obtained do not allow one to check the correspondence of this dependence to Eq. (XIV) due to its complicated character (parameters ε_1 , ε_2 , and γ are also a function of [CumH]).

The combined determination of the effective firstand second-order rate constants of the decomposition of DMDO was performed by integrating Eq. (XIV). The calculations were performed by the equation

$$\ln \frac{k^{(1)} + k^{(2)}[DMDO]}{[DMDO]} = \ln \frac{k^{(1)} + k^{(2)}[DMDO]_0}{[DMDO]_0} + k^{(1)} \cdot t, \quad (XVI)$$

where $k^{(1)} = (1 + e\tau + e/\alpha) \cdot k_{+1} k_4 [\text{CumH}]/(k_{-1} + k_4 [\text{CumH}]), k^{(2)} = \alpha k_{19} k_{21} / (k_{25a} + k_{25b}).$

The $k^{(1)}$ and $k^{(2)}$ values (see Table 4) were determined by minimization of the partial derivatives $\partial t/\partial k^{(1)}$ and $\partial t/\partial k^{(2)}$. The $k^{(1)}$ values are characterized by a large error of determination and, in some cases, have no physical meaning. As in the previous case, this is related to a smaller contribution of the first order consumption of DMDO.

At different initial concentrations of DMDO and $[CumH] = 1.0 \text{ mol } L^{-1}$:

$$k^{(1)} = (2.0 \pm 1.0) \cdot 10^{-3} \text{ s}^{-1}; \ k^{(2)} = 0.37 \pm 0.09 \text{ L mol}^{-1} \text{ s}^{-1}.$$

It is noteworthy that the values of the effective firstorder rate constants obtained by independent methods (in the first case, the determination was performed from the initial rates, and in the second case, from the whole kinetic curve) agree well with each other and are close to the rate constants of the consumption of DMDO

Table 4. Initial rates (w_0) and effective first- $(k^{(1)})$ and second-order $(k^{(2)})$ rate constants for decomposition of dimethyldioxirane induced by alkyl radicals (42 °C, acetone)

[DMD0]-10 ²	[CumH]	$w_0 \cdot 10^4$	k ⁽¹⁾ · 10	$k^{(2)}$
/mol	L ^{-I}	/mol L ⁻¹ s ⁻¹	/s-1	/L mol ⁻¹ s ⁻¹
2.1	1.0	1.39	0.6	0.28
2.9	1.0	2.98		0.46
3.1	1.0	3.26	2.1	0.27
3.2*	1.0	3.33	1.9	0.30
4.1	1.0	6.05	2.3	0.28
5.0	1.0	8.73	1.2	0.37
5.2*	1.0	10.3	3.9	0.31
5.5	1.0	9.7	2.1	0.51
6.2*	1.0	12.5	3.4	0.42
8.4*	1.0	21.5	0.5	0.46
3.6	1.3	4.93	3.6	0.30
3,4	1.5	6.05	2.2	0.50
3.4	1.8	6.28	3.7	0.45

* Oxygen $(-10^{-3} \text{ mol } \text{L}^{-1})$ was initially present in the solution. The reaction rate and concentration of DMDO were determined after "burn-out" of O₂.

measured by the CL method in an atmosphere of O₂. In fact, the k_{eff} value determined by Eq. (IV) coincides with the $k^{(1)}$ parameter of Eq. (XVI) with an accuracy of $(1 + e\tau + e/\alpha)$. It is likely that the $(1 + e\tau + e/\alpha)$ parameter does not differ strongly from 1; therefore, k_{eff} is close to $k^{(1)}$ within the experimental error.

The good agreement between the second-order rate constants favors the suggested mechanism of the reac-



Fig. 3. Dependence of the initial rate of consumption of DMDO on its concentration (42 °C, $[CumH]_0 = 1.0 \text{ mol } L^{-1}$, acetone).

tion and makes it possible to estimate the rate constant of the decomposition of DMDO induced by the alkyl radical. Since chain termination at alkyl radicals occurs with rate constants close to diffusion constants,²⁴ let us accept that $k_{25a} + k_{25b} \approx 5 \cdot 10^9$ L mol⁻¹ s⁻¹, from which $\alpha k_{19}k_{21} \approx 1.7 \cdot 10^9$ L² mol⁻² s⁻². Assuming that $\alpha \approx 0.1 -$ 1 and $k_{19} \approx k_{21}$, we found that the rate constant of the reaction of DMDO with the alkyl radical is equal to ~10⁵ L mol⁻¹ s⁻¹.

Thus, all obtained data on the reaction products and kinetics make it possible to conclude that the consumption of DMDO in its reaction with cumene involves chainradicals. The chain decomposition of dioxirane results in the "barren" consumption of DMDO to cause small yields of the products of the oxidation of cumene per dioxirane converted (see Table 1 and Refs. 3, 6, and 9).

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Received September 18, 1996; in revised form December 3, 1996