Kinetics of the reaction between dimethyldioxirane and 2-methylbutane

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The kinetics of the reaction between dimethyldioxirane and 2-methylbutane in acetone solutions were studied spectrophotometrically at 25 °C. The radical-chain induced decomposition of dioxirane proceeding with the participation of the carbon-centered radicals follows the first-order kinetic law. The reaction is inhibited by dioxygen. In the presence of O_2, the dimethyldioxirane consumption is due to the homolysis of the O—O bond (at a rate constant of $6.3 \cdot 10^{-4}$ s^{-1}) followed by attack of the C—H bond of 2-methylbutane by the biradical formed. The rate constant of the reaction between the alkyl radical and dimethyldioxirane was estimated.

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

The oxidation reactions under the action of dioxiranes, three-membered cyclic peroxides, are fast and selective and proceed under mild conditions.[1–3]

In a number of works,[4–8] it has been concluded that the interaction between dioxiranes and organic compounds proceeds *via* a molecular mechanism. However, convincing proofs of participation of free radicals in these reactions have been obtained recently.[9–15] Thus, the reaction rate decreases substantially in the presence of O_2 and typical inhibitors. The formation of some products (for instance, acetates MeCOOR, where RH is an oxidized substance) can be explained on the basis of the concept of participation of free radicals. Previously,[15] we have shown that the kinetic regularities, the reaction products, chemiluminescence, and thermochemistry of the reaction of dimethyldioxirane (DMDO) with cumene are in line with a radical mechanism, in which the chain decomposition of dioxirane induced by the carbon-centered radicals is a key stage. In continuation of these investigations, the kinetic regularities of the reaction of DMDO with 2-methylbutane were studied in this work.

Experimental

Dimethyldioxirane was synthesized, identified, and analyzed according to the procedure published previously.[3] 2-Methylbutane was purified by successive treatment with conc. H_2SO_4, 5% solution of $NaHCO_3$, and water, then dried with $MgSO_4$ at −10 °C and distilled, b.p. 28 °C. The receiving flask was cooled with snow. The purified 2-methylbutane was stored in sealed ampules at low temperature.

The concentrations of DMDO and 2-methylbutane were varied from 1.3 to $7.1 \cdot 10^{-2}$ mol L^{-1} and from 0.52 to 4.6 mol L^{-1}, respectively. The kinetics of reactions were studied spectrophotometrically by monitoring the DMDO consumption on a Specord M-40 instrument at λ = 335 nm (ε = 10 L mol^{-1} cm^{-1}). A quartz cell (l = 1 cm) containing 0.7 to 1.4 mL of solution of dioxirane in acetone was placed in the chamber of the spectrophotometer and thermostated at 25 °C. Then, the necessary amount of 2-methylbutane (RH) was added. The cell was tightly closed, and the consumption of DMDO was monitored.

Results and Discussion

The kinetics of the reaction of 2-methylbutane with dimethyldioxirane were studied at $[RH]_0 \gg [DMDO]_0$ ($[RH]_0$ and $[DMDO]_0$ are the initial concentrations of the reagents). The kinetic curves of the DMDO consumption (Fig. 1) have an S-shape. Two linear portions

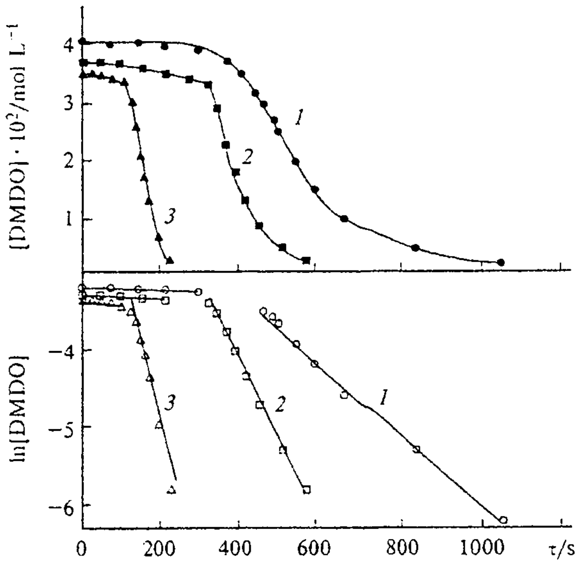


Fig. 1. Kinetic curves of DMDO consumption and their semilogarithmic anamorphoses (with acetone as the solvent, at 25 °C), [RH] = 0.52 (*1*), 2.0 (*2*), and 4.6 mol L^{-1} (*3*).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 1785—1788, October, 1997.

1066-5285/97/4610-1690 $18.00

Table 1. Kinetic data for the reaction between DMDO and 2-methylbutane (with acetone as the solvent, at 25 °C)

$[RH]_0$	$[DMDO]_0$	$k_{eff} \cdot 10^4$	$[DMDO]_\tau \cdot 10^2$	$k_{chain} \cdot 10^2$	τ
mol L^{-1}		$/s^{-1}$	/mol L^{-1}	$/s^{-1}$	/s
—	4.00	0.23	—	—	—
0.52	4.05	1.2±0.5	3.85	0.48±0.02	493
1.00	4.00	2.1±0.1	3.60	0.68±0.03	413
2.00	3.70	3.2±1.1	3.30	1.1±0.1	336
3.00	3.75	3.4±1.5	3.50	1.7±0.2	185
4.60	3.50	4.4±1.7	3.30	2.4±0.3	132
1.00	1.90	2.3±0.2	1.30	0.51±0.04	1880
1.00	7.10	2.3*	6.50	1.3±0.1	275

Note. $[DMDO]_\tau$ is the DMDO concentration at the end of the induction period, τ.

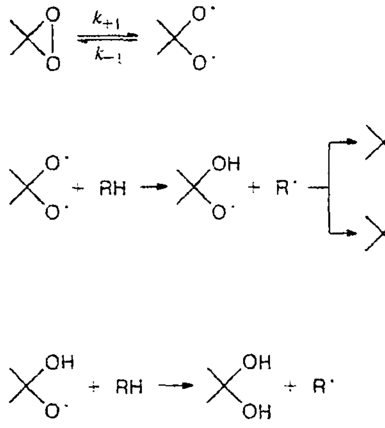
* Estimated from the initial rate of the reaction during the induction period.

are observed on the anamorphosis of the kinetic curve in the first-order coordinates. The rate of the DMDO consumption in the second portion is substantially higher than that in the first portion. The duration of the first portion (the induction period, τ) decreases as the concentrations of the reagents increase (see Fig. 1, Table 1). However, the decrease in the concentration of DMDO during the induction period is nearly the same and is equal to $(4\pm2) \cdot 10^{-3}$ mol L^{-1} irrespective of the initial experimental conditions. This value is comparable with the concentration of dioxygen dissolved in acetone. The initial concentrations of the reagents and the effective rate constants for the DMDO consumption in both the slow and the fast (corresponding to the progressing process) portions of the kinetic curve (k_{eff} and k_{chain}, respectively) are given in Table 1.

The observed kinetic regularities are well explained in the framework of the radical-chain mechanism we proposed previously.[15] The homolysis of the peroxide bond in DMDO followed by the attack of the radical intermediate on the C—H bond of the substrate results in the formation of alkyl radicals. The latter cause a chain-induced decomposition of DMDO, thus sharply accelerating the process. However, the alkyl radicals transform into peroxide radicals in an oxygen atmosphere; the rate constant of this transformation is equal to the diffusion rate constant.[16] The peroxide radicals are inactive in the reaction with DMDO and recombine to terminate the chain. This is evidenced by the fact that the amount of dioxirane consumed during the induction period is independent of the concentrations of the reagents. An increase in the DMDO and RH concentrations results in an increase in the rate of generation of the alkyl radicals and a more efficient chemical binding of oxygen, thus decreasing the induction period.

The obtained experimental data can be described by the sequence of reactions given below.

Initiation. In the absence of RH, the rate constant of decomposition of DMDO (k_{eff}) is equal to $2.3 \cdot 10^{-5}$ s^{-1} and it increases 5 to 20 times as RH is added (see Table 1). This fact makes it possible to neglect the decomposition of the biradical and its consumption in the reaction with the solvent in the presence of RH.



(1)

(2a)

(2b)

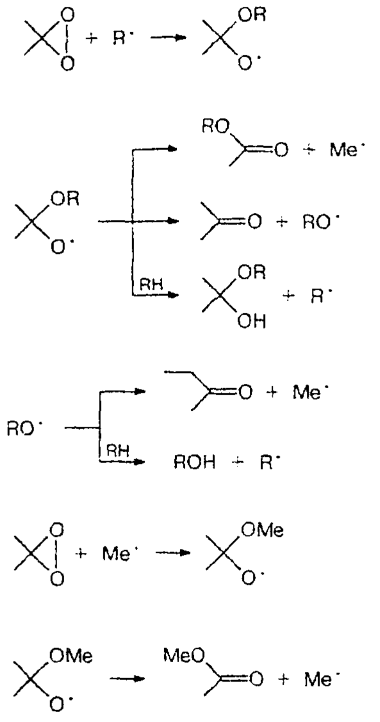
(3)

Reactions of R· radicals in the dioxygen atmosphere

$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$ (4)

$ROO^{\cdot} + ROO^{\cdot} \longrightarrow$ Chain termination (5)

Chain propagation and chain termination reactions in an inert atmosphere



(6)

(7a)

(7b)

(7c)

(8a)

(8b)

(9)

(10)

$R^{\cdot} + Me^{\cdot} \longrightarrow$ Chain termination (11)

Applying the quasi-steady-state principle with respect to the biradical intermediate, we get for the reaction *in the dioxygen atmosphere*

$$-\frac{d[DMDO]}{dt} = \frac{k_{+1}\cdot k_2[RH]}{k_{-1}+k_2[RH]}[DMDO] . \qquad (12)$$

This expression is identical to that describing the experimental dependence of the reaction rate on [DMDO]. It follows from Eq. (12) that the k_{eff} measured in the experiments is equal to

$$k_{eff} = \frac{k_{+1}\cdot k_2[RH]}{k_{-1}+k_2[RH]} . \qquad (13)$$

Equation (13) explains the dependence of the effective rate constant on the concentration of the oxidation substrate (see Table 1), while its anamorphosis (Fig. 2) makes it possible to determine the rate constant of the homolysis of the O—O bond of dioxirane:

$1/k_{+1} = (1.58\pm0.63)\cdot 10^3$ s, and $k_{+1} = 6.3\cdot 10^{-4}$ s^{-1}.

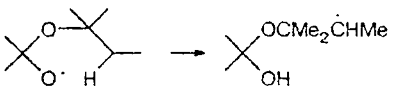
In the absence of oxygen, the reaction rate can be determined from the following equation

$$-\frac{d[DMDO]}{dt} = k_{eff}[DMDO] + k_6[R][DMDO] + $$
$$+ k_9[Me][DMDO]. \qquad (14)$$

Here k_{eff} has the same meaning as above. In Ref. 15, we have performed a detailed analysis of the kinetic scheme of the chain-induced decomposition of DMDO in the quasi-steady-state approximation and found that the rate of consumption of dioxirane is described by the following expression

$$-\frac{d[DMDO]}{dt} = (1 + e/\alpha)k_{eff}[DMDO] +$$
$$+ (\alpha k_6 k_9 k_{11}{}^{-1})[DMDO]^2, \qquad (15)$$

where $e = k_{2a}/(k_{2a} + k_{2b})$ is the probability of escape of the radicals from a solvent cage; α is the probability of formation of the Me$^\cdot$ radical from the α-alkoxyl $Me_2(RO)CO^\cdot$ radical (R is *tert*-pentyl). In our opinion, the observed first order with respect to the concentration of dioxirane does not contradict Eq. (15); at the same time, it indicates that the value of the parameter α is small. The reason is likely that isomerization



(7d)

occurs simultaneously with reactions (7a), (7b), and (7c).

Similar isomerization reactions of alkoxyl radicals resulting in a decrease in the probability of β-decomposition have been described previously.[17] The alkyl radical formed is most likely analogous to the *tert*-pentyl radical in its properties. Since the probability value (α) is small, the contribution of the consumption of DMDO in the second-order reaction decreases while the contribution of the consumption of DMDO in the first-order reaction (the first term of the sum in Eq. (15)) increases simultaneously, which offers the advantage of a first-order reaction with respect to the concentration of DMDO over the analogous second-order reaction. In accordance with the above concept, the effective rate constant in the second portion of the kinetic curve, k_{chain}, increases as the initial concentration of dioxirane increases (see Table 1).

A linear dependence of k_{chain} on the concentration of 2-methylbutane was established experimentally (see Table 1):

$$k_{chain} = (2.1\pm0.4)\cdot 10^{-3} + (4.8\pm0.2)\cdot 10^{-3}[RH],\ r = 0.997.$$

Since the consumption of DMDO in the first-order reaction prevails over that in the second-order reaction, $k_{chain} \approx (1 + e/\alpha)\cdot k_{eff} \approx e\cdot k_{eff}/\alpha$. The RH concentration affects k_{eff} (see Eq. (13)) and α:

$$\alpha = \frac{k_{7a}}{k_7} + \frac{k_{7b}}{k_7}\cdot\frac{k_{8a}}{k_{8a}+k_{8b}[RH]} ,$$

where $k_7 = k_{7a} + k_{7b} + k_{7c}\cdot[RH] + k_{7d}$. An increase in the $1/\alpha$ function most likely compensates a decrease in the rise of k_{eff} as the RH concentration increases (see

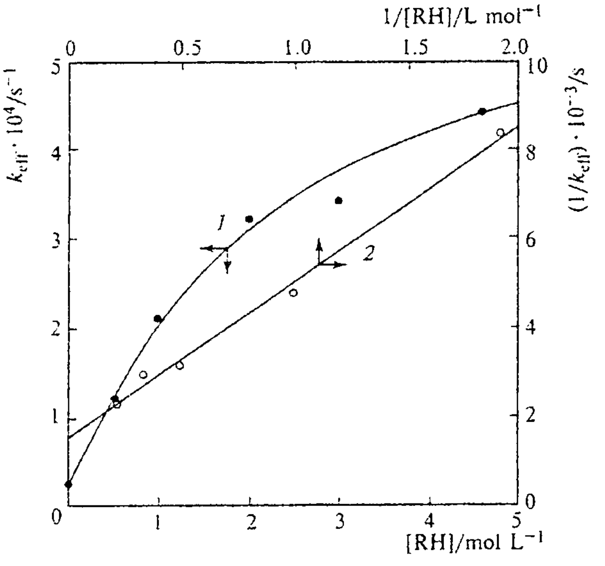


Fig. 2. Dependence of the effective rate constant of DMDO consumption (k_{eff}) on concentration of 2-methylbutane (*1*) and its anamorphosis (*2*).

Fig. 2), thus dictating a linear relationship between k_{chain} and [RH].

Using the experimental data one can calculate approximately the rate constant of the induced decomposition of DMDO (k_{ind}). This constant was estimated under the following assumptions: the reactivities of DMDO in the desired reaction and in the stages of chain propagation ((6) and (9), respectively) are close (*i.e.*, $k_{\text{ind}} \approx k_6 \approx k_9$), while the concentrations of the carbon-centered radicals are approximately equal ([R] ≈ [Me]; the concentrations of the radicals can be calculated from the condition of equality of the rates of initiation (w_i) and termination (w_t): $[R] \approx (w_i/k_t)^{1/2}$; and the rate constant for the recombination of alkyl radicals is close to the diffusion-controlled value:[18] $k_t \approx 5 \cdot 10^9$ mol L^{-1} s^{-1}. In this case we get for the rate of the chain process (w_{chain}):

$$w_{\text{chain}} = k_{\text{chain}}[\text{DMDO}] = k_{\text{ind}}[\text{R}][\text{DMDO}],$$

from which it follows, taking into account that $w_i = 2ek_{\text{eff}}[\text{DMDO}]$, that

$$k_{\text{ind}} = k_{\text{chain}} \cdot k_t^{1/2}/(2e \cdot k_{\text{eff}}[\text{DMDO}])^{1/2}. \qquad (16)$$

The results of calculations of the k_{ind} (mol L^{-1} s^{-1}) values for different values of the probability of escape of the radicals from the solvent cage (e) are given below:

e	0.1	0.2	0.5	0.8	0.9
$k_{\text{ind}} \cdot 10^{-5}$	5.8±2.3	4.1±1.6	2.6±1.0	2.0±0.8	1.9±0.8

The estimates of the k_{ind} value are in reasonably good agreement with the value obtained in Ref. 15 (k_{ind} ~10^5 mol L^{-1} s^{-1}). According to the data reported previously,[13] the rate constant of the reaction of methyl radical with DMDO at 20 °C is approximately equal to 10^6 mol L^{-1} s^{-1}.

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Received January 10, 1997