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 O₂, the dimethyldioxirane consumption is due to the homolysis of the O—O bond (at a rate constant of 6.3·10⁻⁴ 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 alkyi 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 O₂ 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. H₂SO₄, 5% solution of NaHCO₃, and water, then dried with MgSO₄ 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 7.1·10⁻² 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 ≫ [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


1066-5285/97/4610-1690 $18.00 © 1997 Plenum Publishing Corporation
Table 1. Kinetic data for the reaction between DMDO and 2-methylbutane (with acetone as the solvent, at 25 °C)

<table>
<thead>
<tr>
<th>[RH]₀ (mol L⁻¹)</th>
<th>[DMDO]₀ (mol L⁻¹)</th>
<th>kₑff. × 10⁻⁴ (s⁻¹)</th>
<th>[DMDO]₁ (mol L⁻¹)</th>
<th>k.chain × 10² (s⁻¹)</th>
<th>τ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.52</td>
<td>4.00</td>
<td>1.2±0.5</td>
<td>3.85</td>
<td>0.48±0.02</td>
<td>493</td>
</tr>
<tr>
<td>1.00</td>
<td>4.00</td>
<td>2.1±0.1</td>
<td>3.60</td>
<td>0.68±0.03</td>
<td>413</td>
</tr>
<tr>
<td>2.00</td>
<td>3.70</td>
<td>3.2±1.1</td>
<td>3.30</td>
<td>1.1±0.1</td>
<td>336</td>
</tr>
<tr>
<td>3.00</td>
<td>3.75</td>
<td>3.4±1.5</td>
<td>3.50</td>
<td>1.7±0.2</td>
<td>185</td>
</tr>
<tr>
<td>4.60</td>
<td>3.50</td>
<td>4.4±1.7</td>
<td>3.30</td>
<td>2.4±0.3</td>
<td>132</td>
</tr>
<tr>
<td>1.00</td>
<td>1.90</td>
<td>2.3±0.2</td>
<td>1.30</td>
<td>0.51±0.04</td>
<td>1880</td>
</tr>
<tr>
<td>1.00</td>
<td>7.10</td>
<td>2.3</td>
<td>6.50</td>
<td>1.3±0.1</td>
<td>275</td>
</tr>
</tbody>
</table>

Note. [DMDO]₁ 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±2) · 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 (kₑff 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. 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. 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 (kₑff) is equal to 2.3 · 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.

Reactions of R' radicals in the dioxygen atmosphere

R' + O₂ → ROO' (4)

ROO' + ROO' → Chain termination (5)

Chain propagation and chain termination reactions in an inert atmosphere

R' + Me → Chain termination (11)