The ratio of the rate constants for H atom abstraction and β-cleavage for bis-oxyisopropylidene biradical

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The relative reactivity of bis-oxyisopropylidene biradical $^{\cdot}OCMe_2O^{\cdot}$ generated upon homolysis of the O—O bond of dimethyldioxirane was characterized by the ratio of the rate constants for H atom abstraction and β-cleavage: $k_3/k_2 = 0.23\pm0.06$ L mol^{-1} (314 K).

Key words: kinetics, dioxiranes; free radicals.

Convincing evidence was obtained that the reaction of dimethyldioxirane (DMDO) with saturated organic compounds occurs by a radical mechanism[1—8] involving bis-oxyisopropylidene biradical as the key intermediate. This biradical, like other oxyl radicals,[9] tends to undergo β-cleavage and hydrogen atom abstraction.[7,8] In this work, we determined the ratio of the rate constants for these reactions.

Experimental

Acetone and tetrachloromethane were purified by a known procedure.[10] Dimethyldioxirane **1** was synthesized in a specially designed reactor that consisted of a 250-mL three-necked flask equipped with a mechanical stirrer and an air condenser. The condenser was connected to a trap cooled with an *n*-octane—liquid nitrogen mixture (−56 °C). Acetone (15 mL), $NaHCO_3$ (12 g), and water (20 mL) were placed in the reactor, and then oxone ($KHSO_4 \cdot 2KHSO_5 \cdot K_2SO_4$) (25 g) was added. The reaction was conducted for 25 min (T_{react} = 10 °C) under argon with intense stirring under vacuum (~150 Torr). The yellowish solution collected in the cooled trap was dried with magnesium sulfate for 4 h at −56 °C. The solution was distilled *in vacuo* (~45 Torr) at −10 °C into a trap cooled with liquid nitrogen. Dimethyldioxirane was identified and analyzed according to the procedure reported previously.[11] The kinetics of decomposition of compound **1** were monitored by spectrophotometry (Specord M40) measuring the decrease in the optical density (λ = 335 nm) at 41.0±0.5 °C in a 2.6-mL quartz cell (optical path 1 cm) maintained at a constant temperature. The initial concentration of compound **1** varied in the $(0.72—4.32)\cdot10^{-2}$ mol L^{-1} range. Mixtures of acetone and tetrachloromethane in various ratios were used as the solvent. The experiments were carried out in an oxygen atmosphere, which was maintained by continuous introduction of oxygen to the solution. The concentration of oxygen, calculated from published data,[12] ranged from $6.8\cdot10^{-3}$ (acetone) to $1.4\cdot10^{-2}$ mol L^{-1} (tetrachloromethane). It was shown in preliminary experiments that during purging, the content of dimethyldioxirane remained virtually constant.

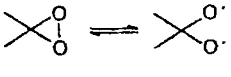
Results and Discussion

Formal kinetics. The kinetics of the thermolysis of compound **1** were studied in an oxygen atmosphere as a function of the $[Me_2CO] : [CCl_4]$ ratio. A decrease in the concentration of acetone retards the thermolysis, indicating the involvement of acetone in the reaction. Under these conditions, the consumption of dioxirane obeys first-order kinetics over the whole concentration range studied. From the kinetic curves, we calculated the effective rate constants (k_{eff}/s^{-1}) of decomposition of **1** as a function of the concentration of acetone (mol L^{-1}):

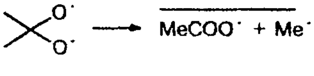
$[Me_2CO]$	13.66	8.69	6.21	1.04	0.55
$k_{eff}\cdot10^5$	2.7±0.3	2.07±0.05	1.58±0.06	0.82±0.01	0.68±0.05

It was found that k_{eff} does not depend on the initial concentration of compound **1**.

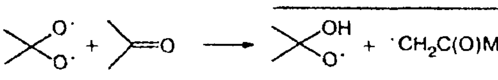
Decomposition mechanism. The kinetic features of the consumption of dioxirane can be explained in terms of the mechanism proposed previously.[7] The steps determining the reaction rate are the following: reversible homolysis of dioxirane at the O—O bond, β-cleavage of bis-oxyisopropylidene biradical, and abstraction of the H atom:



(1)



(2)



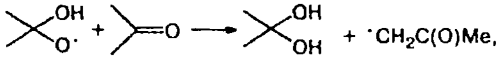
(3)

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1321—1323, July, 1998.

The subsequent reactions result in the formation of carbon-centered radicals, which are rapidly converted into peroxy radicals in the oxygen atmosphere:

$$MeCOO^{\cdot} \longrightarrow Me^{\cdot} + CO_2, \qquad (4)$$

(5)



(6)

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}\ (R = CH_2C(O)Me,\ Me). \qquad (7)$$

Under the conditions chosen, peroxy radicals are inactive in the chain propagation reaction; they do not react with compound **1**[8] but, instead, undergo recombination and terminate the oxidation chain.

Steps (4)—(7) have no effect on the rate of consumption of dioxirane. According to the above-presented mechanism, the rate of the process is

$$-\frac{d[DMDO]}{dt} = \frac{k_{+1}\cdot(k_2 + k_3\cdot[Me_2CO])}{k_{-1} + k_2 + k_3\cdot[Me_2CO]}\cdot[DMDO]. \qquad (8)$$

Apparently, the rate of closure of the dioxirane ring (W_{-1}) is substantially higher than the rate of destruction (W_2) and the rate of hydrogen abstraction by the biradical intermediate (W_3). In this case, the dependence of the effective rate constant for the consumption of compound **1** on the concentration of acetone can be transformed in the linear form:

$$k_{eff} = K_1\cdot k_2 + K_1\cdot k_3\cdot[Me_2CO]. \qquad (9)$$

Equation (9) holds with a high correlation coefficient ($r = 0.995$) (Fig. 1, plot *1*). From the dependence of k_{eff} on the concentration of acetone, the parameters of this equation were calculated:

$K_1\cdot k_3 = (1.5\pm0.2)\cdot10^{-6}$ L mol^{-1} s^{-1},

$K_1\cdot k_2 = (6.4\pm1.5)\cdot10^{-6}$ s^{-1},

$k_3/k_2 = 0.23\pm0.06$ L mol^{-1}.

It is of interest that the corresponding k_a/k_d ratio for the *tert*-butoxy radical, calculated from published data,[13,14] is 5 L mol^{-1}. The lower k_3/k_2 ratio found for bis-oxyisopropylidene biradicals, compared to the corresponding ratio of the rate constants for reactions of *tert*-butoxy radicals, is apparently due to more effective β-cleavage of the biradical. Apparently, the biradical intermediate is more destabilized than the *tert*-butoxy radical as shown by the increased k_2 value and, correspondingly, the decreased k_3/k_2 ratio.

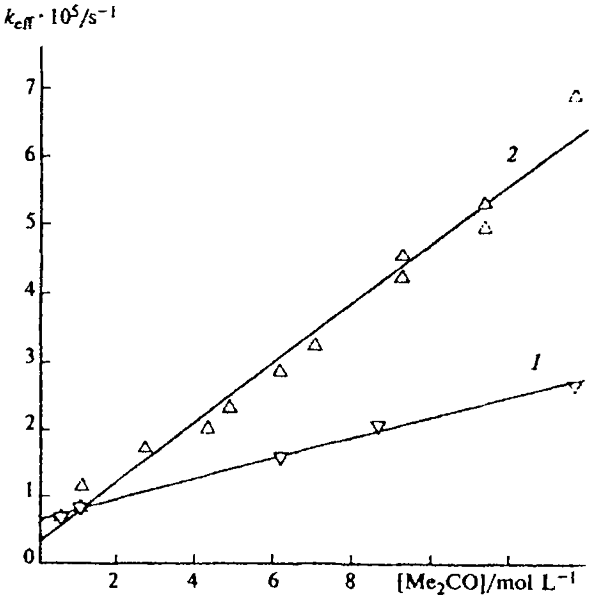


Fig. 1. Dependence of the effective rate constant (k_{eff}) of the thermolysis of **1** on the concentration of acetone: freshly prepared solution of **1** (*1*); after storage for 7 days (*2*).

Note that when dioxirane was stored for 7 days at −56 °C (with short thaws needed to take aliquot samples), its concentration decreased from 0.1 to 0.09 mol L^{-1}. The pattern of dependence of k_{eff} on the concentration of acetone changed accordingly (see Fig. 1, plot *2*). The increase in k_{eff} is obviously due to the fact that products of decomposition of compound **1** with more flexible H atoms appear in the acetone solution. In our opinion, this accounts for the increase in the rate of consumption of **1** in the presence of products of its decomposition, which has been observed earlier.[15]

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