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Kinetics of the Thermal Decomposition of 1,2-Dioxaspiro[2,5]octane

S. A. Grabovskii, E. A. Markov, E. G. Galkin, and N. N. Kabal'nova
Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Ufa, 450054 Bashkortostan, Russia
e-mail: stas_g@anrb.ru

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Abstract—The products and kinetics of the thermolysis of 1,2-dioxaspiro[2,5]octane in cyclohexanone and cyclohexanone–CCl_4 mixtures are studied. 1,2-Dioxaspiro[2,5]octane is consumed via two parallel routes: isomerization to oxepan-2-one and solvent (cyclohexanone) oxidation with the partial escape of radicals from the cage (17% at 25°C). Under an inert atmosphere, the alkyl radicals formed by solvent oxidation initiate the chain radical decomposition of 1,2-dioxaspiro[2,5]octane. The mechanism of 1,2-dioxaspiro[2,5]octane thermolysis is discussed on the basis of the results obtained. The activation parameters of 1,2-dioxaspiro[2,5]octane isomerization to oxepan-2-one and reactions of dioxaspiro[2,5]octane with cyclohexanone are discussed.

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INTRODUCTION

Strained cyclic peroxides (dioxiranes) are widely used in organic chemistry for the oxidation of compounds of various classes [1, 2]. Dioxiranes can efficiently be used only if their stability and conversion mechanisms are known. A number of dioxiranes have been synthesized to date [3]. However, works devoted to the dioxirane decomposition kinetics and products are scarce. Data on the decomposition products of dioxirane (H_2CO_2) [4, 5], methyl(trifluoromethyl)dioxirane [6], dimesityldioxirane [7, 8], and 1,2-dioxaspiro[2,5]octane [9] have been published. Thermolysis kinetics was studied for dimethyl- [10] and methyl(ethyl)dioxiranes [11].

Earlier [10, 11], we carried out a detailed study of the kinetics and thermolysis products of dimethyl- and methyl(ethyl)dioxiranes. The major products of their decomposition at room temperature and at lower temperatures are the corresponding esters. An additional reaction channel appears at higher temperatures, which is the oxidation of CH bonds of the solvent. Solvent oxidation generates radicals in the system. The yield of the radicals for acetone oxidation by dimethyldioxirane is 0.23 at 56°C, and that for 2-butanone oxidation by methyl(ethyl)dioxirane is 0.43 at 35°C. Under an inert atmosphere, dimethyldioxirane decomposes via the chain radical mechanism induced by the alkyl radicals.

The homolysis of the O–O bond of the three-membered cycle with the formation of an unstable biradical is common for the thermal decomposition of dioxiranes. The decomposition mechanism of this biradical depends on the substituents. The solvent and temperature affect the thermolysis process. The following data on 1,2-dioxaspiro[2,5]octane are available from the literature: its decomposition at –25°C in cyclohexanone yields oxepan-2-one; as the temperature is raised, the latter decomposes rapidly to form oligomers [9].

In the present work, we report the thermolysis of 1,2-dioxaspiro[2,5]octane in cyclohexanone and its mixtures with CCl_4, including the kinetics of 1,2-dioxaspiro[2,5]octane decomposition. The DFT (B3PW91) simulation of the homolysis of the O–O bond of selected dioxiranes is presented.

EXPERIMENTAL

NMR spectra were recorded on a Bruker AM300 spectrometer (Me_4Si standard, $(D_3C)_2CO$ and $CDCl_3$ as the solvents). UV–vis spectra were recorded on a Specord M40 double-beam spectrophotometer (Carl Zeiss Jena). GC/MS analyses were carried out on an HP5890 Series II chromatograph (capillary column HP-5, $l = 30$ m) with an HP5972 mass-selective detector. Quantitative analysis was performed on an HP5890E Series II chromatograph (capillary column HP-5, $l = 30$ m).

Cyclohexanone (**1**) was dried over molecular sieve A4 and was distilled under argon prior to use. Tetrachloromethane (reagent grade) was purged with an ozone–oxygen mixture until a stable blue color appeared. Next, ozone was blown out with an inert gas and tetrachloromethane was distilled. 1,2-Dioxaspiro[2,5]octane (**2**) was synthesized according to the standard procedure [12]. Water was frozen out of dioxirane solutions at –30°C. The dioxirane concentration was determined by iodometric titration. The molar extinction coefficient of compound **2** was derived from iodometric titration data and the absorbance of its solutions at the absorption peak wavelength ($\varepsilon_{345\,\text{nm}}$ = 12.9 l mol^{-1} cm^{-1}). The consumption kinetics of **2** was studied spectrophotometrically in temperature-controlled quartz cells (l = 0.5 or 1 cm) by measuring the decreasing absorbance at $\lambda_{\max}$ = 345 nm between 8 and 70°C. The initial dioxirane concentration was varied from 0.1 to 0.2 mol/l. Before the beginning of the reaction, the solution was purged with oxygen for 2 min. The oxygen concentration in **1** was determined as described in [13]. The solubility of oxygen between 13 and 70°C is temperature-independent and is $(6.2 \pm 0.1) \times 10^{-3}$ mol/l, coinciding with the earlier published value (6.3×10^{-3} mol/l at 20°C) [14]. The quantitative analysis of the resulting peroxides was carried out by iodometric titration [15].

The products were analyzed by GC/MS and GLC after the complete decomposition of **2**. After the light products were analyzed, the solvent was evaporated on a rotary evaporator and the residue was separated in a column with neutral alumina using hexane–*tert*-BuOMe mixtures with a gradient of 8 : 1 to 1 : 9 as the eluent. The resulting substance was analyzed by ^{1}H NMR spectroscopy. The spectrum indicated the presence of two oligomers with different terminal groups at the carbonyl fragment (Fig. 1).

The ^{1}H NMR spectrum of the oligomer with the cyclohexan-2-onyl fragment exhibits multiplets H(2) at 5.12–5.24 ppm and H(3,4,5,6) at 5.6–1.9 ppm. However, the peak area of the signal is not equal to that of the triplet at 0.89 ppm from the terminal CH_3 group. This suggests the presence of a second oligomer presumably having a terminal acidic group. The other ^{1}H NMR signals are assigned to both oligomers ($CDCl_3$, 300 MHz): 1.15–1.5, 1.5–1.3 (m, $(C\underline{H}_2)_3CH_2C(O)O$); 2.31 (t, J = 7.45 Hz, $C\underline{H}_2C(O)O$); 4.07 (t, J = 6.58 Hz, $C(O)OCH_2$).

DFT calculations were performed using a combination of the three-parameter hybrid exchange Becke functional (B3) [16] with the PW91 correlation functional [17], which is hereafter designated B3PW91. The standard two-exponential 6-31+G(d) basis set [18] was used. As was shown earlier, this method provides good agreement between calculated and experimental data [19]. All geometric parameters for the molecules, intermediates, and transition states were optimized without symmetry constraints. The nature of the optimized structures was determined by an analysis of the eigenvalues of the Hesse matrix, which is the matrix of the second derivatives of energy with respect to coordinates. The coordinates were calculated geometrically. The calculated energies were corrected for the zero-point energies (ZPE) of the corresponding structures taken without a correction factor. The influence of nonspecific interactions of the solvent on the thermodynamic parameters was estimated by the polarized continuum method using the COSMO procedure [20].

All quantum-chemical calculations were performed using the NWChem program package [21].

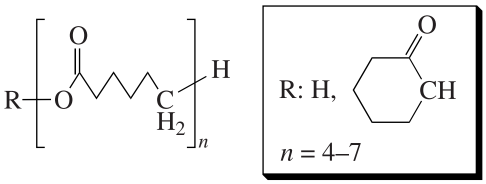


Fig. 1. Structure of the oligomers resulting from the decomposition of **2**.

RESULTS AND DISCUSSION

Decomposition Products of 1,2-Dioxaspiro[2,5]octane

The decomposition of **2** in oxygen-saturated solutions of **1** gives oxepan-2-one as the major product throughout the temperature range examined, and 1,2-cyclohexanedione was also observed at 50°C. These results are in full agreement with the results of earlier studies of the decomposition products [9]. In deoxygenated solutions, the decomposition is accompanied by intense warming and results in the formation of oligomers (Fig. 1). A hydroperoxide was observed after the complete decomposition of dioxirane **2** in oxygen-saturated solutions of **1**. The hydroperoxide yield in terms of consumed dioxirane was 1 and 5% at 19 and 45°C, respectively.

Kinetics of 1,2-Dioxaspiro[2,5]octane Thermolysis in an Oxygen Atmosphere

The thermolysis of **2** was studied in a solution of **1** in an oxygen atmosphere. As compared to a dimethyldioxirane solution in acetone [10] and to a methyl(ethyl)dioxirane solution in butan-2-one [11], dioxirane **2** in a solution of **1** is much less stable. The conversion of **2** in an oxygen atmosphere at 30°C in 3 h is 93%. The kinetic profiles of the consumption of **2** in a cyclohexanone solution are *S*-like (Fig. 2), which was observed for dimethyl- and methyl(ethyl)dioxiranes during the decomposition in solutions of the corresponding ketones [10, 11]. Purging the dioxirane solution with an inert gas for 1 min decreases the oxygen concentration and thus shortens the induction period (Fig. 2). However, up to the point of its sharp increase, the reaction rate is the same as in the experiments in which a constant O_2 concentration in the solution was maintained throughout the measurement time. Similar kinetic features of the thermal decomposition of dioxiranes were observed earlier [10, 11]. This is due to the fast conversion of the alkyl radicals in the presence of oxygen into peroxy radicals, which decay via recombination. In the absence of oxygen, the alkyl radicals ini-

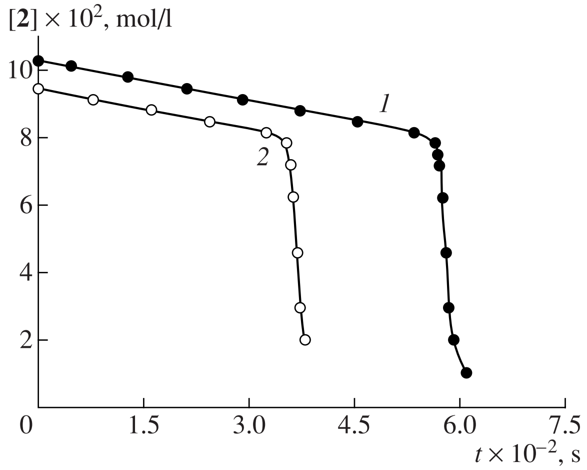


Fig. 2. Typical kinetic profiles of the thermolysis of **2** in a solution of **1** (35.9°C). Before measurements, the solution was purged with (*1*) oxygen and (*2*) argon.

tiate the chain radical decomposition of the dioxirane, as is indicated by the formation oligomers (Fig. 1) under these conditions.

The kinetic profiles of the thermolysis of **2** in oxygen are linearizable with a high correlation coefficient in the coordinates of a first-order equation. The apparent rate constant of the thermolysis of **2** (k_{app}) is independent of the concentration of **2**. The temperature effect on k_{app} was studied in the temperature range from 8 to 41°C (Fig. 3). The overall activation parameters of the decomposition of **2** (in cyclohexanone as the solvent) were calculated from this temperature dependence:

$$\log k_{app} = (10 \pm 1) - (78 \pm 4)/\theta,$$
$$r = 0.994; \quad \theta = 2.303RT, \text{ kJ/mol}.$$

The composition of the decomposition products indicates that a reaction between **2** and **1** occurs. To estimate the contribution from this reaction to the thermal decomposition of **2**, we studied the thermolysis reaction in **1**–CCl_4 mixtures. In the carbon tetrachloride medium, the apparent rate constant of the consumption of **2** is smaller and depends linearly on the concentration of **1** (Fig. 4): $k_{app} = k_{isom} + k_{ox}[\mathbf{1}]$.

The rate constants of the isomerization of **2** (k_{isom}) and of its reaction with **1** (k_{ox}) were derived from the dependences of k_{app} on the concentration of **1** at different temperatures (Table 1). The dependence of the apparent rate constant of thermolysis on the concentration of **1** is consistent with the competition taking place between the monomolecular and bimolecular channels of the consumption of **2** (which was deduced from the analysis of the products).

A similar dependence was observed for the decomposition of dimethyl- and methyl(ethyl)dioxiranes [10, 11].

The activation parameters for the isomerization of **2** to oxepan-2-one and for its reaction with **1** are as follows:

$$\log k_{isom} = (12 \pm 2) - (94 \pm 1)/\theta, \quad r = 0.999,$$
$$\log k_{ox} = (7 \pm 1) - (69 \pm 2)/\theta,$$
$$r = 0.999; \quad \theta = 2.303RT, \text{ kJ/mol}.$$

Of the dioxiranes studied to date, dioxirane **2** is the least stable. These data are quite consistent with the parameters calculated theoretically at the B3PW91/6-31+G(d) level for the rate-determining step of dioxirane isomerization, namely, O–O bond homolysis yielding an intermediate biradical (Table 2). The dipole moments of **2** and the transition state are similar

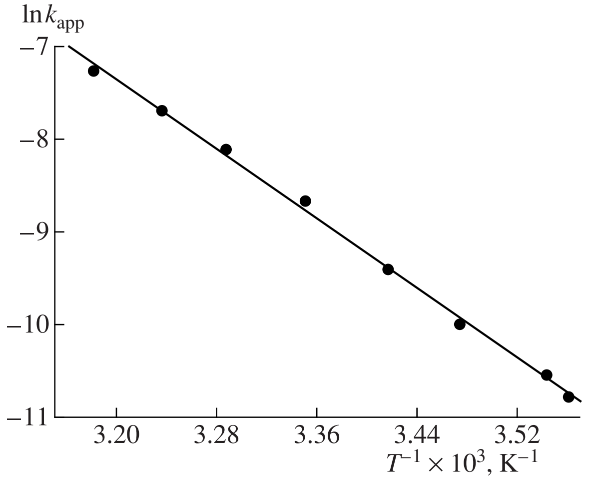


Fig. 3. Temperature dependence of the apparent rate constant of the thermolysis of **2** (8–41°C, cyclohexanone as the solvent).

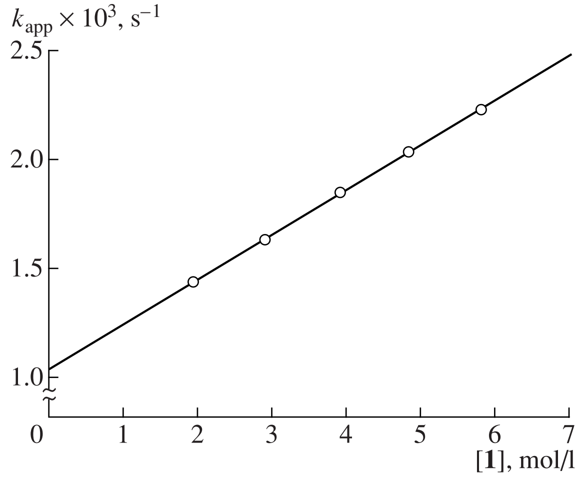
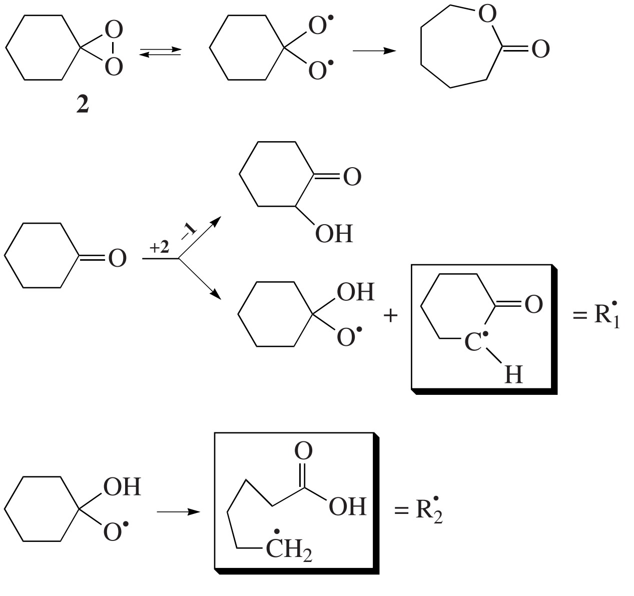


Fig. 4. Apparent rate constant of the thermolysis of **2** versus the concentration of **1** (63.5°C).

(3.39 and 3.31 D, respectively). This is due to the fact that only slight geometric changes take place on passing from the reactant to the transition state. According to the B3PW91/6-31+G(d) calculations within the polarization continuum model, the change in the free Gibbs energy for the transfer of the reaction from the gas to the condensed phase is 0.19 kcal/mol for CCl_4, 0.20 for acetone, and 0.21 for MeCN. The ratios of the isomerization constants for **2** in the solvents at 25°C were calculated to be $k_{MeCN}/k_{CCl_4} = 1.03$ and $k_{acetone}/k_{CCl_4} = 1.01$.

The radical escape to the bulk (ξ) for cyclohexanone oxidation by dioxirane **2** for a series of temperatures, determined using the procedure described in [10, 11], is 0.17 (25°C), 0.19 (31°C), 0.22 (36°C), and 0.25 (41°C). We demonstrated earlier that the radical and nonradical routes of the interaction of dioxiranes with C–H bonds have a common radical-type transition state [19]. Since the radical escape to the bulk increases with increasing temperature in the same way as in the decomposition of the standard radical initiators (e.g., AIBN [22]), the increase in ξ is probably due to the fact that the radical escape from the solvent cage increases with increasing temperature because of the decreasing viscosity. A similar phenomenon was observed for adamantane oxidation by dimethyldioxirane [23]. This is confirmed by the linear dependence of $(1 - \xi)^{-1}$ on $T^{1/2}\eta^{-1}$ in Noyes' cage effect theory (Fig. 5) [24].

The data obtained in this study can be represented in terms of the following main steps of the process:



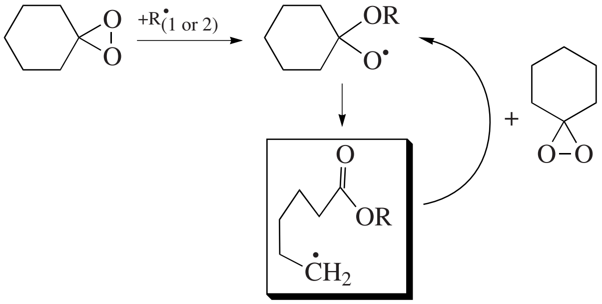
Scheme 1.

Table 1. Rate constants of the isomerization of **2** (k_{isom}) and of the reaction between **2** and **1** (k_{ox}) during the thermolysis of **2** in cyclohexanone–CCl_4 mixtures

T, °C	$k_{isom} \times 10^5$, s^{-1}	$k_{ox} \times 10^5$, l mol^{-1} s^{-1}
27.9	2.0 ± 0.2	1.0 ± 0.1
36.3	5.6 ± 1.0	2.2 ± 0.2
54.0	38 ± 4	10 ± 1
63.5	104 ± 12	21 ± 3
69.3	201 ± 37	26 ± 3

Throughout the temperature range examined, the major decomposition product of **2** in oxygen is oxepan-2-one, which results from dioxirane isomerization through the formation of the intermediate bis(oxy)cyclohexylidene biradical. Another channel of the consumption of **2** is solvent oxidation proceeding via a radical transition state capable of forming both radicals and products of oxygen insertion into the C–H bond (alcohols [19] and, then, ketones [25]). In the presence of oxygen, the alkyl radicals are transformed into peroxy radicals, which recombine, but do not initiate a chain radical process, and only an insignificant part of them attacks the solvent to form trace amounts of hydroperoxides.

For deoxygenated solutions, the alkyl radical route can be presented as follows:



Scheme 2.

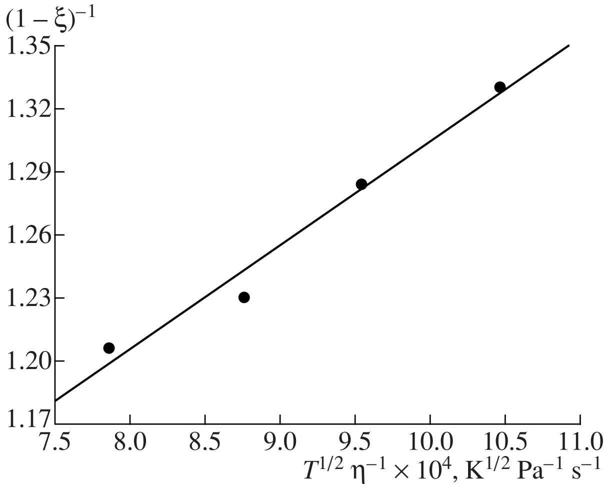


Fig. 5. Plot of $(1 - \xi)^{-1}$ versus $T^{1/2}\eta^{-1}$ for the oxidation of **1** by dioxirane **2** (**1** as the solvent).

Table 2. Thermodynamic parameters of the isomerization of selected dioxiranes calculated at the B3PW91/6-31+G(d) level compared with experimental values of $\Delta G^{\neq}_{298}$ and the rate constant

Dioxirane*	$\Delta H^{\neq(\mathrm{theor})}_{298}$, kJ/mol	$\Delta S^{\neq(\mathrm{theor})}_{298}$, J K^{-1} mol^{-1}	$\Delta G^{\neq(\mathrm{theor})}_{298}$, kJ/mol	$\Delta G^{\neq(\mathrm{exp})}_{298}$, kJ/mol	k_{isom}(25°C), s^{-1}
DMD	94.3	6.3	92.4	108.1 [10]	2.0×10^{-7} [10]
MED	93.7	–1.5	93.8	106.9 [11]	1.1×10^{-6} [11]
2	91.5	0.5	91.3	98.5	3.3×10^{-5}
TFM	88.4	–2.2	89.0	98.9 [6]	2.3×10^{-5} [6]

* DMD is dimethyldioxirane, MED is methyl(ethyl)dioxirane, and TFM is methyl(trifluoromethyl)dioxirane.

The interaction of the alkyl radicals with dioxirane yields oxy radicals, which isomerize to form alkyl radicals, which then react with **2** to regenerate the oxy radicals. This results in oligomers, which are the major products of the decomposition of **2** in deoxygenated solutions of **1**.

Thus, the change of the substituents at the 1,2-dioxocyclopropane fragment exerts a substantial effect on the thermal stability of dioxiranes.

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