Kinetics and Catalysis, Vol. 45, No. 6, 2004, pp. 809–812. Translated from Kinetika i Kataliz, Vol. 45, No. 6, 2004, pp. 859–862.

PEROXIDES-XI

The Role of Free Radicals in the Reaction of Dimethyldioxirane with Adamantane

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Received August 22, 2003

Abstract—The products and the kinetics of the reaction of dimethyldioxirane with adamantane in CCl_4 were studied. It was found that the reaction simultaneously occurred via molecular and radical paths. The contribution of the radical process was 65% at 30.6°C. The activation parameters of the reaction of dimethyldioxirane with adamantane in the presence of an inhibitor were determined: $\log k = (7.33 \pm 0.14)–(58.5 \pm 0.8)/\Theta$, $\Theta = 2.3RT$(kJ/mol) (10.3–69.3°C).

INTRODUCTION

Dioxiranes, which are highly reactive three-membered cyclic peroxides, can hydroxylate the C–H bonds of aliphatic hydrocarbons under mild conditions. Oxidation with the participation of dioxiranes occurs with high regioselectivity. Studies on the mechanism of oxidation by dioxiranes are of continuous interest.

Several opinions on the mechanism of dioxirane reactions with alkanes have formed to date: the "insertion" of an oxygen atom [1–3], the homolysis of dioxirane at the O–O bond followed by hydrogen abstraction from the substrate by the resulting biradical or the homolysis of dioxirane by the alkane molecule [4, 5], the simultaneous occurrence of the above mechanisms [6], and the parallel occurrence of two reactions (through the same [7] or different transition states). One of these reactions results in molecular products, whereas the other produces a radical pair in a solvent cage [7–9]. Data on the oxidation of compounds containing cyclopropane fragments, which can undergo isomerization with high rate constants with the formation of radicals at the β-position with respect to the cyclopropane ring [1, 10], demonstrated the domination of the "insertion" reaction. However, note that the direction of the reaction depends on the structure of the substrate oxidized and the conclusions made are true only for the test compounds. The extension of the mechanism found for these specific alkanes to other substrates is somewhat premature.

The kinetics and the products of adamantane oxidation by dioxirane were studied in the most detail [11, 12]. It was concluded that the reaction occurs via the insertion mechanism.

In this work, we found that adamantane oxidation by dimethyldioxirane (DMDO) occurs with the participation of free radicals.

EXPERIMENTAL

Acetone (analytical grade) and tetrachloromethane (high-purity grade) were subjected to a single distillation in an efficient column. Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) from Aldrich® was used without additional purification. DMDO was synthesized using a published procedure [13]. DMDO was extracted into CCl_4 in accordance with a previously developed procedure [14] (the residual amount of acetone was ~0.1 mol/l). The concentration of DMDO in CCl_4 was varied over the range 0.03–0.15 mol/l. Adamantane from Aldrich® was twice sublimed.

The kinetics of the reaction of DMDO with adamantane in CCl_4 were measured by spectrophotometry at $\lambda = 335$ nm ($\varepsilon_{max} = 14$ l mol^{-1} cm^{-1}) over the temperature range 10.3–69.3°C. The reactor was a thermostatted quartz cell (of volume 1.1 ml; $l = 0.5$ cm) with a ground-glass stopper. Oxygen was passed through the reaction mixture for ~1.5 min before the beginning of an experiment; next, the cell was closed with the stopper. The concentration of O_2 in the CCl_4–hydrocarbon binary system was calculated from published data [15]. The initial concentration of adamantane was varied over the range 0.15–0.9 mol/l.

RESULTS AND DISCUSSION

We studied the kinetics and the products of the reaction of adamantane (AdH) with DMDO. The reaction products and their proportions (table) are analogous to data obtained previously in the oxidation of adamantane by DMDO in acetone [12] with the exception of

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Reaction products in the oxidation of adamantane with DMDO in CCl_4

Product	Yield, %
1-AdOH	94*
1,3-Ad(OH)$_2$	3*
Ad=O	1*
AcOH	60**

Note: 15°C; $[DMDO]_0 = 0.078$ mol/l; $[AdH]_0 = 0.156$ mol/l; adamantane conversion, 49%.

* Yield on a consumed AdH basis.

** Yield on a consumed DMDO basis.

acetic acid, which was detected in the products of this reaction for the first time. Moreover, our kinetic data indicate regions of sharp acceleration. Figure 1 demonstrates a typical DMDO consumption curve in the reaction with adamantane; this curve has a marked induction period. We found that the $[O_2]_0/\Delta[DMDO]$ ratio was constant at a given temperature and independent of the initial concentrations of adamantane and DMDO. The experimental data are well reproducible; this fact excludes the assumption that the effect was due to the contamination of reactants or the reactor surface. When oxidation was performed in an open vessel, an acceleration region was not observed because of the diffusion of oxygen from the environment to the solution. Thus, we were dealing with a radical process, in which oxygen was an inhibitor. Because DMDO is incapable of forming radicals by thermolysis in CCl_4 [8], the reaction is initiated by the interaction of adamantane with DMDO. In general, the experimental data can be explained by the scheme given below.

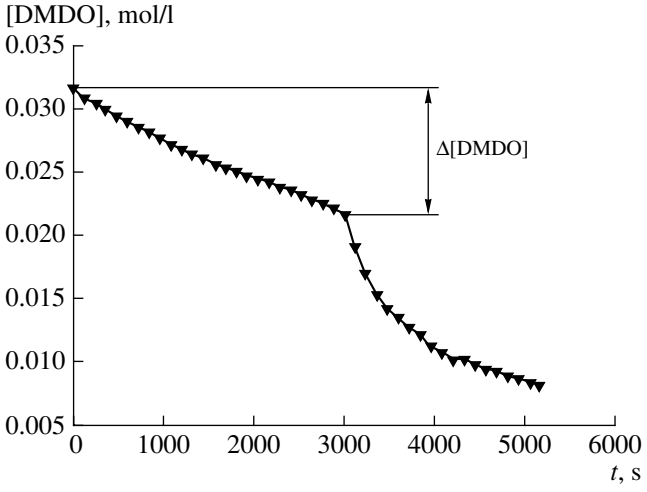
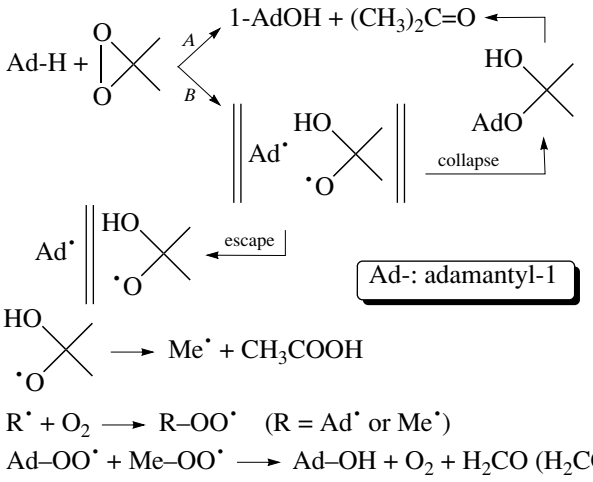


Fig. 1. DMDO consumption in adamantane oxidation ($[AdH]_0 = 0.82$ mol/l; $[O_2]_0 = 6 \times 10^{-3}$ mol/l; $T = 15$°C).



$R^\bullet + O_2 \longrightarrow R\text{–}OO^\bullet$ (R = Ad$^\bullet$ or Me$^\bullet$)

$Ad\text{–}OO^\bullet + Me\text{–}OO^\bullet \longrightarrow Ad\text{–}OH + O_2 + H_2CO\ (H_2CO^*)$

Scheme.

The high yield of 1-AdOH in this process is indicative of the predominance of the cross recombination of 1-adamantyl peroxy (1-AdOO$^\bullet$) and methyl peroxy (MeOO$^\bullet$) radicals with the formation of corresponding tetraoxides, which undergo decomposition in accordance with the Russell mechanism. This conclusion also follows from an analysis of the rate constants of the recombination reactions of the peroxy radicals. The rate constant of the recombination of methyl peroxy radicals is higher than that of 1-AdOO$^\bullet$ by several orders of magnitude ($k_{MeOO^\bullet} = 1 \times 10^8$ l mol^{-1} s^{-1}, 295 K [16]; $k_{AdOO^\bullet} \approx k_{t\text{-}BuOO^\bullet} = 1 \times 10^4$ l mol^{-1} s^{-1}, 297 K [17]). Consequently, the steady-state concentration of 1-AdOO$^\bullet$ is

$$[AdOO^\bullet] = [MeOO^\bullet](k_{MeOO^\bullet}/k_{AdOO^\bullet})^{1/2},$$

$$[AdOO^\bullet] \approx 160[MeOO^\bullet].$$

Unfortunately, rate constant data for the cross recombination of primary peroxy radicals with tertiary peroxy radicals are insufficient. An analysis of data on the cross recombination of radicals of this kind demonstrated that the rate constant of this reaction was lower than the rate constants of the recombination of primary peroxy radicals by a factor of 10–100 [18–20]. For the MeOO$^\bullet$ + *t*-BuOO$^\bullet$ reaction, the rate constant is 2×10^6 l mol^{-1} s^{-1} (293 K) [19]. This value is sufficient for the predominance of cross recombination.

In the case of the recombination reactions of peroxy radicals, excited products can be formed. Indeed, the process was accompanied by weak chemiluminescence (CL) in the visible region of the spectrum at ~450 nm. The rate constants of CL decay were consistent with the reaction rate constants measured by spectrophotometry; this fact provides support for the hypothesis of the participation of free radicals in the process.

Let us consider the contribution from reaction path *B* (see scheme) to the oxidation of AdH by DMDO. The process is a simple example of the complete inhibition of a radical chain process, and O_2 is a free-radical acceptor. Consequently, the rate of O_2 consumption is proportional to the rate of initiation (without considering latent radical processes) and the consumed amount of inhibitor provides an opportunity to determine the efficiency of initiation [8]. Because the stoichiometry of oxygen consumption in the radical process is 1 : 1 with respect to DMDO, the ratio $[O_2]_0/\Delta[\text{DMDO}] = \xi$ is the fraction of processes that lead to the formation of free radicals.

The ratios between the molecular and radical reaction paths in the oxidation of adamantane by DMDO in CCl_4 at different temperatures are given below:

T, °C	30.6	40.2	59.2
ξ*	0.65 ± 0.02	0.71 ± 0.02	0.75 ± 0.02

* The fraction of the radical reaction path.

The calculated values of ξ demonstrated that the contribution of the radical path was considerable; it is not improbable that it was even higher because of latent radical processes. However, it is not to be assumed that the oxidation of all alkanes by DMDO is dominated by a radical mechanism. Preliminary results suggest that, even in the case of alkanes, ξ can vary over a wide range. We found that $\xi \approx 0$ for the oxidation of *exo-endo-endo*-heptacyclo[9.3.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{12,14}$]pentadecane by DMDO.

It is likely that the weak increase in ξ with temperature (see above) was due to the increasing escape of radicals from the solvent cage rather than the fact that the activation energy for path *B* is higher than that for path *A*. It is likely that reaction paths *A* and *B* have either a common transition state or transition states with similar energies.

The apparent rate constants derived from the semilogarithmic anamorphoses of the DMDO consumption curves for the reaction with adamantane in the presence of oxygen are adequately linearized on the k_{app}–$[\text{AdH}]_0$ coordinates (Fig. 2). The bimolecular reaction rate constants obtained for the oxidation of adamantane by DMDO in CCl_4 are given below.

T, °C	10.3	20.1	30.6	40.2	49.5	59.2	69.3
$k \times 10^3$, l mol^{-1} s^{-1}	0.339	0.866	1.79	3.76	7.68	13.2	25.0

They are somewhat lower than the published values of 2.98×10^{-3} l mol^{-1} s^{-1} (25°C) [11] and $(2.83–3.30) \times 10^{-3}$ l mol^{-1} s^{-1} (20°C) [12]. This is likely due to the different polarity of solvents or the decrease in the proton-donor ability of the solvent.

Based on the above data, we calculated the activation parameters of the oxidation of adamantane with DMDO in CCl_4: $\log k = (7.33 \pm 0.14)–(58.5 \pm 0.8)/\Theta$, $\Theta = 2.3RT$ (J/mol); $r^2 = 0.999$. A low value of the activation entropy ($S^{\neq}_{298} = –26.9 \pm 0.5$ J mol^{-1} K^{-1}) indicates a highly ordered transition state.

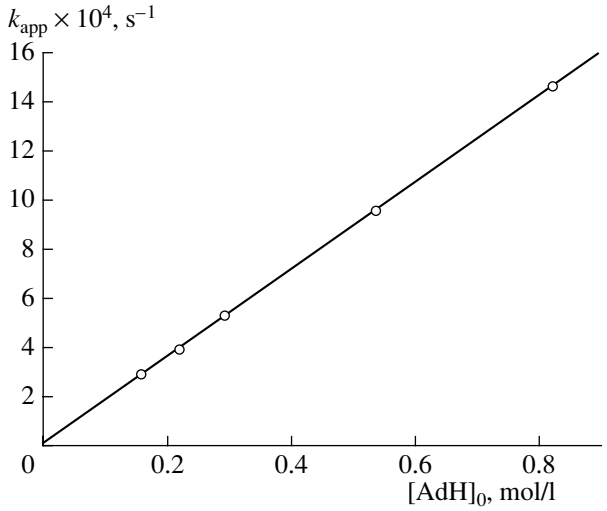


Fig. 2. Dependence of the apparent rate constant of the reaction of adamantane with DMDO in CCl_4 on adamantane concentration at 30.6°C.

Thus, with the use of the reaction of DMDO with adamantane, we demonstrated that the oxidation of alkanes by DMDO can simultaneously occur via two reaction paths (*A* and *B*), one of which gives a radical pair and the other leads to nonradical products. Both of the reaction paths have either one transition state or transition states with similar energies. The authors of previous publications did not observe the above-described behavior because of the low solubility of adamantane in acetone (the maximum concentration of adamantane in acetone is commensurable with the concentration of oxygen in solution). The replacement of acetone by CCl_4 allowed us to increase the concentration of adamantane significantly and to find the true mechanism of the reaction.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Support of Domestic Science.

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