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Kinetics of oxidation of fullerene C_{60} with dimethyldioxirane

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The kinetics of the reaction of dimethyldioxirane with fullerene C_{60} was studied, and the activation parameters $\log k = (8.3\pm0.8) - (14.2\pm0.9)/\theta$, ($\theta = 2.3RT$ kcal mol^{-1}) (20—45 °C) were determined. The formation of paramagnetic particles was detected.

Key words: dimethyldioxirane, fullerene, kinetics, oxidation, free radicals.

Fullerene dioxide and other oxidation products are of practical use.[1] Dioxiranes are widely employed for the oxidation of various organic compounds. Two mechanisms of this reaction, molecular and radical, are discussed.[2] Fullerene C_{60} is oxidized with dimethyldioxirane (**1a**) slowly (~12 h, 25 °C) with a conversion of at most 10%. The reaction products are the epoxide and 1,3-dioxolane derivative of fullerene with yields of 40 and 60%, respectively.[3] A biradical mechanism of formation of the 1,3-dioxolane derivative has been proposed.[3] However, this mechanism is highly improbable because of fast isomerization of the biradical, which fact was confirmed by the high-level quantum-mechanical calculation.[4] Methyl(trifluoromethyl)dioxirane (**1b**) reacts with C_{60} faster than **1a**: time of reaction is 5—6 min and fullerene conversion is 72%. A mixture of oxides: monoxide, dioxide (two isomers), and trioxide (mixture of isomers) are formed with yields of 67, 30, and 8%, respectively, whereas the 1,3-dioxolane derivative of fullerene[5] was not found.

This work is aimed at the study of the kinetics of oxidation of C_{60} by dimethyldioxirane.

Experimental

Acetone (analytical grade) and tetrachloromethane (high purity grade) were distilled on an effective column. Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) (Aldrich) was used without additional purification. Dimethyldioxirane (**1a**) was synthesized according to a conventional method,[6] and solutions obtained were analyzed according to a known procedure.[7] According to a previously developed procedure,[8] dimethyldioxirane was extracted with CCl_4 (residual amount of acetone ~0.1 mol L^{-1}). Concentrations of **1a** were varied within $1.27 \cdot 10^{-2}$—$3.17 \cdot 10^{-2}$ mol L^{-1}. Fullerene C_{60} was used in a CCl_4 solution, $[C_{60}]_0 = 2.08 \cdot 10^{-5}$ mol L^{-1}. The reaction kinetics was studied by changes in optical density of C_{60} at $\lambda = 330$ nm. The absorption spectra were recorded on a Specord M-40 spectrophotometer. The ESR spectra were recorded on a SE/X 2544 spectrometer. The quantitative analysis of radical was performed with the use of 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-3-oxide-1-oxyl as a reference sample, and g_x-factor was measured relative a signal of diphenylpicrylhydrazyl. The reaction products were analyzed on a Bruker AM-300 NMR spectrometer with a working frequency of 300 MHz (solvent was $CDCl_3$ or benzene-d$_6$).

Procedure for oxidation of fullerene C_{60}. The equimolar amount of a solution of **1a** was added to a solution of fullerene in CCl_4. After the reaction was completed, the solvent was evaporated on a rotary evaporator until a precipitate began to form (solution volume decreased by ~5 times). A mixture obtained was stored for 20 h, and the precipitate was separated and dissolved immediately in CCl_4 or benzene. The paramagnetic particles were detected by ESR. No paramagnetic particles were found in the filtrate. The solvent was removed on a rotary evaporator and the residue was dissolved in $CDCl_3$. The signals typical of $C_{60}O$ and the 1,3-dioxolane derivative of fullerene[3] were found in the ^{1}H and ^{13}C NMR spectra of the solution.

Results and Discussion

The reaction kinetics was studied at the ratio of concentrations $[\mathbf{1a}]_0 \gg [C_{60}]_0$. The kinetic curves with the correlation coefficient $r > 0.98$ are described by the first-order equation with respect to C_{60}. The apparent first-order rate constants $k_{app} = k[\mathbf{1a}]^n$ were calculated from the anamorphoses of the kinetic curves. The linearity of the plot k_{app} *vs.* $[\mathbf{1a}]_0$ indicates the first order with respect to dioxirane (Fig. 1). The kinetic equation is as follows:

$$-d[C_{60}]/dt = k[\mathbf{1a}][C_{60}],$$

where k is the second-order rate constant.

The activation parameters of the reaction were calculated from the temperature dependence

$$\log k = (8.3\pm0.8) - (14.2\pm0.9)/\theta,$$

where $\theta = 2.3RT$ (kcal mol^{-1}) at 20—45 °C.

Conversion of fullerene at the equimolar ratio of the reactants in CCl_4 at 24 °C is 80—90%, which is much

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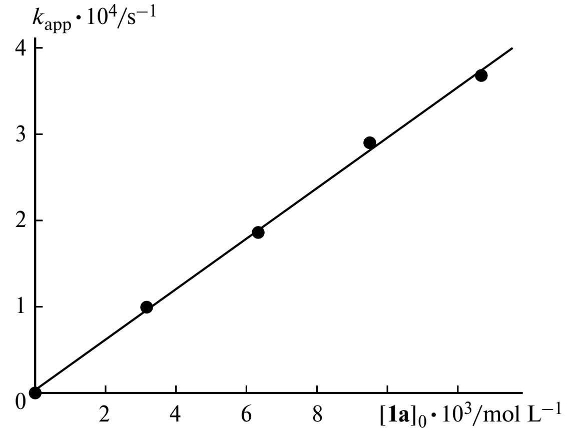


Fig. 1. Plot for the apparent reaction rate constant (k_{app}) *vs.* initial concentration of dimethyldioxirane **1a** (43 °C, solvent CCl_4).

higher than that in the earlier reported work.[3] This is due to the fact that the reaction was conducted in CCl_4, which solvent is inert toward **1a**.[2] Toluene that was used as a solvent in the cited work[3] was oxidized under the reaction conditions, resulting in the ineffective consumption of **1a**.

When an excess of the oxidizing agent was used and the ratio $[\mathbf{1a}]/[C_{60}]$ was higher than 1.2, the signals of di- and triepoxides of fullerene were observed in the ^{13}C NMR spectrum, as also they were found in fullerene oxidation with trifluorodimethyldioxirane.[5]

Along with epoxide $C_{60}O$ and the 1,3-dioxolane derivative found earlier,[3] paramagnetic particles were detected. The ESR signal (Fig. 2) was observed both at the equimolar ratio of the reactants and at the 100-fold excess of dimethyldioxirane. In both cases, the ESR signal is a symmetrical singlet (g = 2.0024; 25 °C). g-Factor of the radical found is close to that of the fullerene radical cation.[9] Note that the oxidation of pyrene with dioxirane **1b** is also accompanied by the formation of a radical species, the pyrene radical cation.[10]

When the amount of the oxidizing agent is increased, the yield of the radical based on the consumed fullerene increases from 0.1 ($[C_{60}]$: [**1a**] = 1 : 1) to 22% ($[C_{60}]$: [**1a**] = 1 : 100). When the sample is cooled to 77 K, a shape of the ESR signal changes reversibly (see Fig. 2). After storing the dry sample for 3 months at ~20 °C, the intensity of the ESR signal was halved.

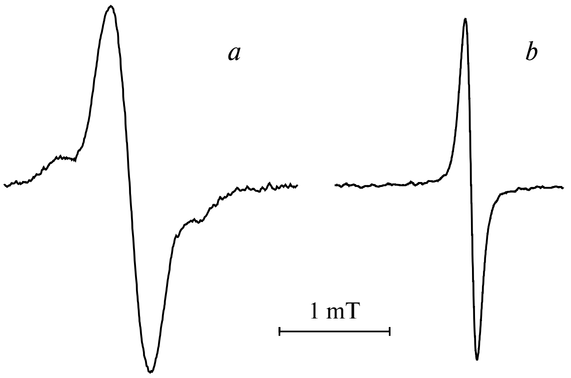


Fig. 2. ESR signal of the adduct of fullerene C_{60} with dimethyldioxirane in CCl_4 at 77 (*a*) and 298 K (*b*).

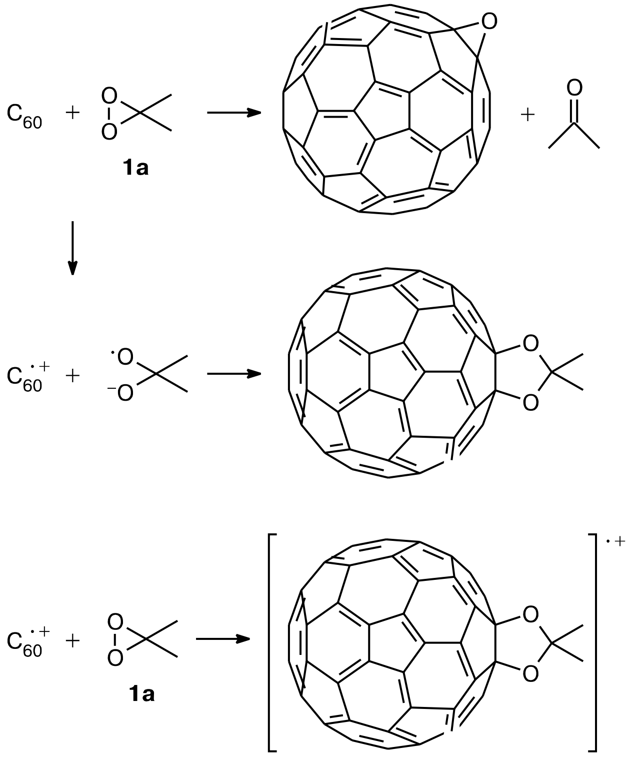
The yields of the radical at different temperatures and at the ratio $[C_{60}]$: [**1a**] = 1 : 100 are presented below. A slight decrease with temperature in the yield of the radical is likely due to a significant acceleration of fullerene epoxidation, which produces no radical.

T/°C	22	36	50
Yield (%)	22±1	22±1	19±1

Thermolysis of **1a** can be neglected under these conditions because the rate constant of thermal decay k_d = $8.0 \cdot 10^{-6}$ s^{-1} at 50 °C in CCl_4.[2]

The proposed reaction mechanism is shown in Scheme 1. However, the fullerene radical cation is a reactive particle,[9] and, hence, the signal observed likely corresponds to the radical cation of oxyfunctionalized fullerene. Thus, fullerene oxidation is an additional example of the dimethyldioxirane reactions, which lead to radical formation.

Scheme 1



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