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Brief Communications

Reactivity of fullerene C_{60} towards peroxy radicals generated by liquid-phase oxidation of cumene and ethylbenzene with oxygen

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The inhibiting action of fullerene C_{60} on the liquid-phase initiated oxidation of cumene and ethylbenzene was studied. The apparent rate constants of inhibition by fullerene C_{60} of cumene and ethylbenzene oxidation were determined by measuring the amount of absorbed oxygen: $(1.3\pm0.2)\cdot10^3$ and $(2.0\pm0.3)\cdot10^3$ L mol^{-1} s^{-1}, respectively.

Key words: fullerene C_{60}, inhibition of oxidation, peroxy radical.

Published data on the ability of fullerene C_{60} to inhibit chemical and biochemical oxidation processes are contradictory.[1] We have earlier found[1] by the volumetric and chemiluminescence methods that fullerene C_{60} manifests no noticeable properties of an inhibitor of the liquid-phase oxidation with oxygen of a series of hydrocarbons with the active C—H bond at the secondary carbon atom. Inactivity of C_{60} as an inhibitor was associated with the predominant occurrence of competitive reactions of radicals $RO_2^{\bullet}$ with hydrocarbon and disproportionation of $RO_2^{\bullet}$. At the same time, the long-wavelength (maxima at 645 and 685 nm) chemiluminescence (CL) presumably attributed to the thermal decomposition of fullerene peroxides (products of the reaction of C_{60} with radicals $RO_2^{\bullet}$) was observed[2] during the initiated oxidation of ethylbenzene (**1**) taken in low concentrations

$$RO_2^{\bullet} + RH \xrightarrow{k_2} ROOH + R^{\bullet},$$

$$RO_2^{\bullet} + RO_2^{\bullet} \xrightarrow{k_6} R'{=}O + ROH + O_2.$$

Such different conclusions about the reactivity of C_{60} towards radicals $RO_2^{\bullet}$, under the conditions of liquid-phase oxidation of hydrocarbons, could be due to a higher sensitivity of the CL method compared to volumetry. Therefore, one of the tasks of the present work was the repeated attempt to find the effect of inhibition by fullerene of ethylbenzene oxidation using precision volumetry. It is known[3] that the disproportionation of a series of tertiary radicals $RO_2^{\bullet}$ proceeds in a different manner than the reaction of secondary radicals

$$RO_2^{\bullet} + RO_2^{\bullet} \xrightarrow{k_6} ROOR + O_2$$

and is characterized by considerably lower values of k_6. Therefore, the stationary concentration of radicals $RO_2^{\bullet}$ in the reaction sulution is substantially higher for the oxidation of hydrocarbon with the active C—H bond at the tertiary carbon atom.[3] This fact increases the probability of addition of $RO_2^{\bullet}$ to a molecule of C_{60}. In this regard, the aim of the work is also the study of the reactivity of C_{60}

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towards tertiary radicals $RO_2^{\cdot}$ generated by the liquid-phase initiated oxidation of cumene and the determination of the apparent inhibition rate constants (fk_{in}) for the addition to C_{60} of peroxy radicals $PhCH(Me)O_2^{\cdot}$ and $PhC(Me)_2O_2^{\cdot}$ generated by the oxidation of ethylbenzene (**1**) and cumene (**2**), respectively.

Experimental

Commercial fullerite C_{60} (99.8%, G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhny Novgorod, Russia), benzene and ethylbenzene (reagent grade) were used without additional purification. Cumene was purified using a known procedure,[4] and the initiator of oxidation α,α′-azobis(isobutyronitrile) (AIBN) was recrystallized according to a procedure described.[5] The inhibition properties of C_{60} were studied on the known[6] model reactions of the initiated oxidation of ethylbenzene (**1**) ($[\mathbf{1}]_0 = 4.9$ mol L^{-1}) and cumene (**2**) ($[\mathbf{2}]_0 = 4.3$ mol L^{-1}) in benzene at the initiation rate (W_i) equal to $9.0 \cdot 10^{-8}$ L mol^{-1} s^{-1}, which was calculated by the known[3] equation

$$W_i = 1.2 \cdot 1.58 \cdot 10^{15} \cdot e^{-(30800/RT)}[\text{AIBN}].$$

Oxidation was carried out in a temperature-controlled glass reactor at 343±0.1 K with continuous magnetic stirring. The amount of absorbed oxygen was determined by the volumetric method ($\Delta V = \pm 0.02$ mL) using temperature-controlled burettes 1 and 2 mL in volume. The efficiency of the inhibiting action of C_{60} was estimated by the degree of decreasing the initial rate of hydrocarbon oxidation due to the addition of a solution of C_{60} in benzene. Synthetic inhibitor 2,6-di-*tert*-butyl-4-methylphenol (ionol) (high-purity grade, N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences) was used as a reference. The procedure of CL measurement[3] and the technique for CL spectra recording[7] were described.

Results and Discussion

It is known that one of the features of the radical chain oxidation process is the possibility of its sharp retardation by the introduction of small amounts of an inhibitor (InH). The decrease in the oxidation rate of the substrate is due to the known[8] reactions of accepting of $RO_2^{\cdot}$ radicals

$$RO_2^{\cdot} + InH \longrightarrow ROOH + In^{\cdot},$$

$$RO_2^{\cdot} + In^{\cdot} \longrightarrow P,$$

where P are products.

The introduction of fullerene additives into the oxidized mixture also decreases the initial rate of oxidation of cumene (**2**), as it is seen from Fig. 1 showing the dependence of the initial rate of oxygen absorption on the concentration of C_{60}. In addition, for the oxidation of cumene (**2**), the addition of C_{60} to the reaction solution results in a sharp decrease in the CL intensity and then its recovery to the level observed in the absence of C_{60} (Fig. 2). Similar changes in CL are also observed upon the addition of the known inhibitors.[3,9]

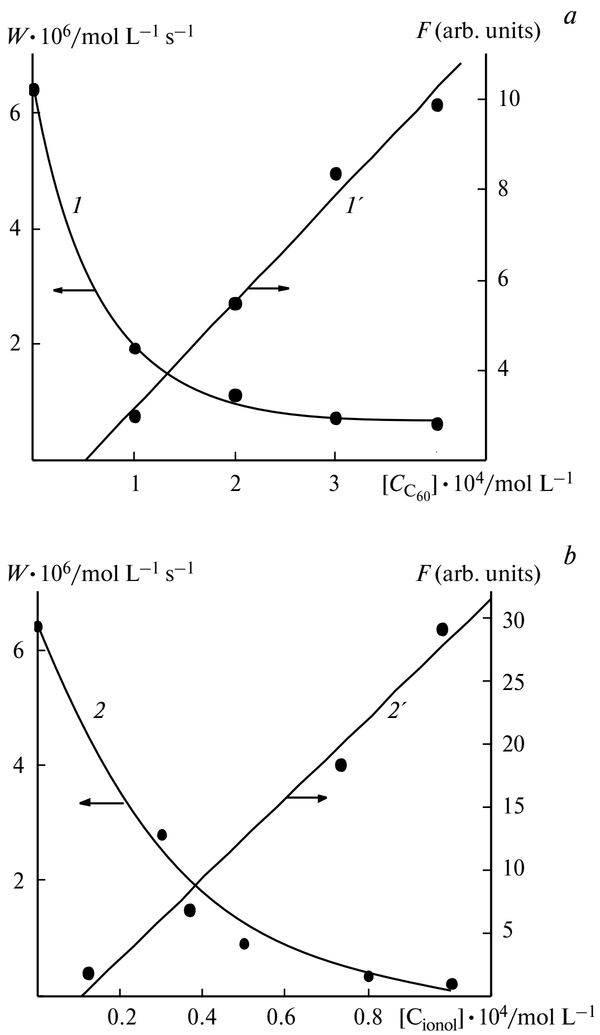

Fig. 1. Initial rate constant of cumene oxidation W (*1*, *2*) and the inhibition parameter F (*1′*, *2′*) *vs* concentrations of fullerene C_{60} (*a*) and ionol (*b*); $W_i = 9 \cdot 10^{-8}$ L mol^{-1} s^{-1}, $T = 343$ K.

For the estimation of the inhibition ability of C_{60}, the apparent rate constant of inhibition fk_{in} (f is the capacity of the inhibitor, and k_{in} is the rate constant of oxidation chain termination on the inhibitor) was determined using the known[9] Eq. (1)

$$F = \frac{W_0}{W_x} - \frac{W_x}{W_0} = fk_{in}[\text{In}]\sqrt{2k_6W_i}, \qquad (1)$$

where [In] is the inhibitor concentration (mol L^{-1}); W_0 and W_x are the initial rate constants of O_2 absorption in the absence and presence of the inhibitor, respectively; W_i is the initiation rate; and F is the inhibition parameter.

Processing of the experimental data on the influence of C_{60} on the initial rate of O_2 absorption in the coordinates of Eq. (1) gave the linear dependence of the inhibition parameter F on the concentration of C_{60} (correlation coefficient $R = 0.99$). The value of fk_{in} was de-

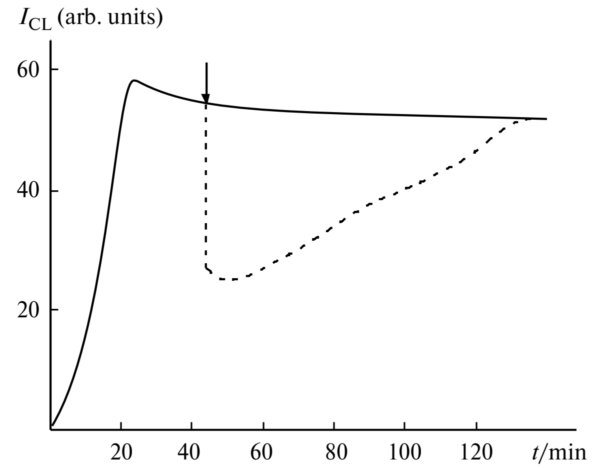

Fig. 2. Chemiluminescence kinetics during the initiated oxidation of cumene. Dashes show the run of the kinetic curve after the addition of fullerene C_{60} ($C = 4 \cdot 10^{-5}$ mol L^{-1}) to the solution; the moment of addition of C_{60} is shown by arrow, $W_i = 9 \cdot 10^{-8}$ L mol^{-1} s^{-1}, $[\mathbf{2}]_0 = 4.3$ mol L^{-1}, $T = 343$ K.

termined from the slope ratio of this dependence. Inserting the value of k_6 known[10] for cumylperoxy radicals ($2k_6 = 3 \cdot 10^4$ L mol^{-1} s^{-1}, $T = 343$ K) into Eq. (1), we obtained the value of the apparent rate constant of inhibition of oxidation of cumene (**2**) by fullerene C_{60} $fk_{C_{60}} = (1.3\pm0.2) \cdot 10^3$ L mol^{-1} s^{-1}. The value of inhibition of oxidation of cumene (**2**) by the efficient inhibitor ionol was determined for comparison under similar conditions (see Fig. 1): $k_{\text{ionol}} = (2.1\pm0.2) \cdot 10^4$ L mol^{-1} s^{-1} (according to Ref. 11, $k_{\text{ionol}} = (2.0\pm0.3) \cdot 10^4$ L mol^{-1} s^{-1}).

To obtain more clear and complete pattern of the processes occurring during organic substrate oxidation in the presence of fullerene, we also studied the action of C_{60} on the oxidation of ethylbenzene (**1**). No inhibition of the oxidation of hydrocarbons with the C—H bond at the secondary carbon atom, including **1**, has been observed earlier[1] by the volumetric method (the accuracy of determination of the volume of absorbed O_2 was $\Delta V = \pm 1$ mL). In the present work, using more precision volumetry ($\Delta V = \pm 0.02$ mL), we found that fullerene C_{60} inhibits, nevertheless, the initiated oxidation of **1**. Thus, the introduction of C_{60} into the solution during the oxidation of **1** induces a noticeable decrease in the oxidation rate. The value of $fk_{C_{60}} = (2.0\pm0.3) \cdot 10^3$ L mol^{-1} s^{-1} determined for the oxidation of ethylbenzene (**1**) differs insignificantly from $fk_{C_{60}}$ obtained for cumene (**2**). Thus, we may conclude that the reactivity of fullerene C_{60} depends slightly on the nature of the peroxy radical. This conclusion is consistent with the results of quantum chemical calculations[12]: the calculated value of the rate constant of addition of the simplest peroxy radical $MeO_2^{\cdot}$ to C_{60} was $3.9 \cdot 10^3$ L mol^{-1} s^{-1}.

The HPLC data also confirm the participation of fullerene C_{60} in the reaction with intermediates of hydrocarbon oxidation (radicals $R^{\cdot}$ and $RO_2^{\cdot}$). For example, the peak of C_{60} decreases ($\tau_{\text{ret}} = 6.87$ min) during the inhibited oxidation of **1** and **2**. We assume that the decrease in the fullerene concentration in the reaction solution is due, to a greater extent, to the addition of radicals $RO_2^{\cdot}$ to C_{60}. This conclusion is based on the published data,[3,9] according to which during the initiated oxidation of hydrocarbons all radicals $R^{\cdot}$ are transformed into $RO_2^{\cdot}$ at $[O_2] \geq 10^{-3}$ mol L^{-1}. In the present work, we measured for the first time the apparent rate constants of inhibition for the initiated oxidation of **1** and **2** with fullerene C_{60}. Thus, it was shown for the oxidation of **1** and **2** that fullerene C_{60} more efficiently retards the rate of oxidation (monitored by O_2 absorption) of the C—H bond at the tertiary carbon atom than that at the secondary carbon atom.

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