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Inertness of C_{60} fullerene toward $RO_2^{\bullet}$ peroxy radicals

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The reactivity of fullerene C_{60} toward peroxy radicals $RO_2^{\bullet}$ was tested by the chemiluminescence method. A comparison of the influence of C_{60} and known inhibitors on the kinetics of liquid-phase chemiluminescence (CL) during oxidation of a series of hydrocarbons (ethylbenzene, cyclohexane, *n*-dodecane, and oleic acid) shows that the fullerene does not react with the $RO_2^{\bullet}$ radicals. A sharp decrease in the CL intensity observed upon C_{60} addition is caused by the quenching of CL emitters with fullerene but not by inhibition of hydrocarbon oxidation.

Key words: fullerene C_{60}, peroxy radicals, chemiluminescence, quenching.

Fullerene C_{60} is named the "radical sponge" due to its ability to efficiently add free radicals of different chemical nature to form fullerenyl radicals[1—3]:

$$C_{60} + X^{\bullet} \rightarrow XC_{60}^{\bullet}, \qquad (1)$$

$X^{\bullet} = R^{\bullet}, RO^{\bullet}, (RO)_2(O)P^{\bullet}$.

Then the fullerenyl radicals dimerize and/or add an additional amount of radicals.[2] Radicals $X^{\bullet}$ are usually prepared by photolysis or thermolysis of compounds belonging to different classes. At the same time, published data on the reactivity of fullerene C_{60} toward peroxy radicals $RO_2^{\bullet}$ are scarce and contradictory. For instance, the reviews on the reactions of C_{60} with free radicals[2] and other reagents[1,4] contain no data on the interaction of C_{60} with the $RO_2^{\bullet}$ radicals. Fullerene C_{60} was found to inhibit the thermooxidative destruction (TOD) at 200—300 °C of poly(methyl methacrylate) (PMMA),[5—7] polystyrene,[5] and copolymers of methyl methacrylate (MMA) with methacrylamides.[8] The antioxidant activity of C_{60} during TOD of these polymers was presumably attributed[7] to the reaction

$$R_iO_2^{\bullet} + C_{60} \rightarrow R_iO^{\bullet} + C_{60}O, \qquad (2)$$

R_i is macroradical.

The work[9] and site of the Pushchino Scientific Center of the Russian Academy of Sciences* reported the inhibition effect on the peroxide oxidation of lipids by fullerene C_{60} bound in a complex with polyvinylpyrrolidone. In this case, reactivity of C_{60} toward free radicals was measured by procedures of nitroblue-tetrasolium reduction and chemiluminescence (CL) arising in peroxide oxidation of lipids. The results of using the first method indicate that the fullerene had no antioxidative properties. However, a decrease in the overall CL intensity in the presence of fullerene C_{60} suggested[9] its inhibition ability.

The above facts and an important role of the $RO_2^{\bullet}$ radicals in oxidative chemical and biochemical processes[10,11] and inhibition effect of fullerene C_{60} on living activities of different viruses and pathogenic bacteria[4,12,13] show that the study of antioxidative properties of C_{60}, namely, the reactivity toward radicals $RO_2^{\bullet}$, is an urgent problem.

In this work, the reactivity of fullerene C_{60} toward peroxy radicals was studied by the CL method. The efficiency of the CL method in studying activity of inhibitors has previously been shown[14,15] for the oxidation of different classes of hydrocarbons.

Experimental

Commercial fullerite, whose purity (C_{60} 99.8%) was monitored by HPLC and elemental analysis, was used. Ethylbenzene (EB), *o*-dichlorobenzene (DCB), *n*-dodecane (DD), and cyclohexane (CH) (chromatographically pure) and oleic acid (OA, edible quality) were used without additional purification. Initiators of oxidation, *viz*., α,α´-azobisisobutyronitrile (AIBN) and dicyclohexyl peroxydicarbonate (DCHPC) and CL activators (hereinafter A), *viz*., 9,10-dibromoanthracene (DBA) and europium(III) 1,10-phenanthroline-tris(thenoyltrifluoroacetonate) ($Eu(TTA)_3 \cdot phen$), were synthesized and purified by recrystallization as described above.[16,17] α-Tocopherol (Aldrich, 97%) and 2,6-di-*tert*-butyl-4-methylphenol (ionol, pure) were used as inhibitors (InH) of oxidation. Solutions of C_{60} were prepared by dissolution of a weighed sample of fullerite in EB or DD—DCB, CH—DCB, and OA—DCB mixtures. These mix-

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tures were used due to low solubility of C_{60} in DD, CH, and OA. The reactivity of C_{60} toward radicals $RO_2^{\bullet}$ was tested using a known method[18] by the influence on the intensity of CL arising upon oxidation with oxygen (in the absence and presence of AIBN and A additives) of several hydrocarbons, such as EB, DD, CH, and OA. The technique and procedures of CL measurement and HPLC have been described earlier.[19,20] The contribution of the internal filter effect caused by CL absorption with fullerene was estimated from a decrease in the emission intensity of a reference radioluminescent light source. The CL absorption did not exceed 20% at $[C_{60}]_{max} = 1.8 \cdot 10^{-3}$ mol L^{-1} and 0.5—5% at $[C_{60}] = 4.8 \cdot 10^{-5}$—$4.5 \cdot 10^{-4}$ mol L^{-1}.

Results and Discussion

Before studies of the influence of fullerene on CL, we tested the effect of the known hydrocarbon inhibitors on the CL intensity during oxidation of hydrocarbons using EB and CH as examples. Note that the CL during oxidation of EB, CH, and OA has been described previously,[18,21] while that for DD oxidation was found in this work. The addition of solutions of inhibitors with an almost constant level of CL intensity results in a sharp decrease in the CL intensity, after which the emission level increases to the initial value (Fig. 1). A similar pattern of changing the CL intensity is observed for addition of the inhibitors to the reaction solutions of DD and OA (the corresponding curves are omitted). The recovery time of the CL intensity is inversely proportional to the efficiency and concentration of the inhibitors. Although the CL intensity of CH takes much longer time for complete recovery (more than 1 h) than that for EB, the intensity begins to rise immediately after the sharp decrease in CL. These results agree completely with known data,[14,16,18] according to which the processes that occur during hydrocarbon oxidation are described by Scheme 1 (the variant using AIBN as an initiator is presented).

Scheme 1

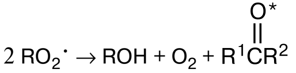
$$\mathrm{AIBN} \rightarrow \mathrm{r}^{\bullet} \qquad (3)$$

$$\mathrm{r}^{\bullet} + \mathrm{O_2} \rightarrow \mathrm{rO_2}^{\bullet} \qquad (4)$$

$$\mathrm{rO_2}^{\bullet} + \mathrm{RH} \rightarrow \mathrm{rOOOH} + \mathrm{R}^{\bullet} \qquad (5)$$

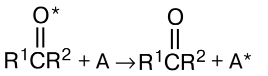
$$\mathrm{R}^{\bullet} + \mathrm{O_2} \rightarrow \mathrm{RO_2}^{\bullet} \qquad (6)$$

$$\mathrm{RO_2}^{\bullet} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}^{\bullet} \qquad (7)$$



$$2\,\mathrm{RO_2}^{\bullet} \rightarrow \mathrm{ROH} + \mathrm{O_2} + \mathrm{R^1}\overset{\overset{\mathrm{O^*}}{\|}}{\mathrm{C}}\mathrm{R^2} \qquad (8)$$

$$\mathrm{RO_2}^{\bullet} + \mathrm{InH} \rightarrow \mathrm{ROOH} + \mathrm{In}^{\bullet} \qquad (9)$$



$$\mathrm{R^1}\overset{\overset{\mathrm{O^*}}{\|}}{\mathrm{C}}\mathrm{R^2} + \mathrm{A} \rightarrow \mathrm{R^1}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{R^2} + \mathrm{A}^* \qquad (10)$$

The $RO_2^{\bullet}$ radicals formed due to the sequence of reactions (3)—(6) disproportionate (see Eq. (8)) to form triplet-excited ketones,[16] which are the primary CL emitters. In the presence of activators A, the energy is trans-

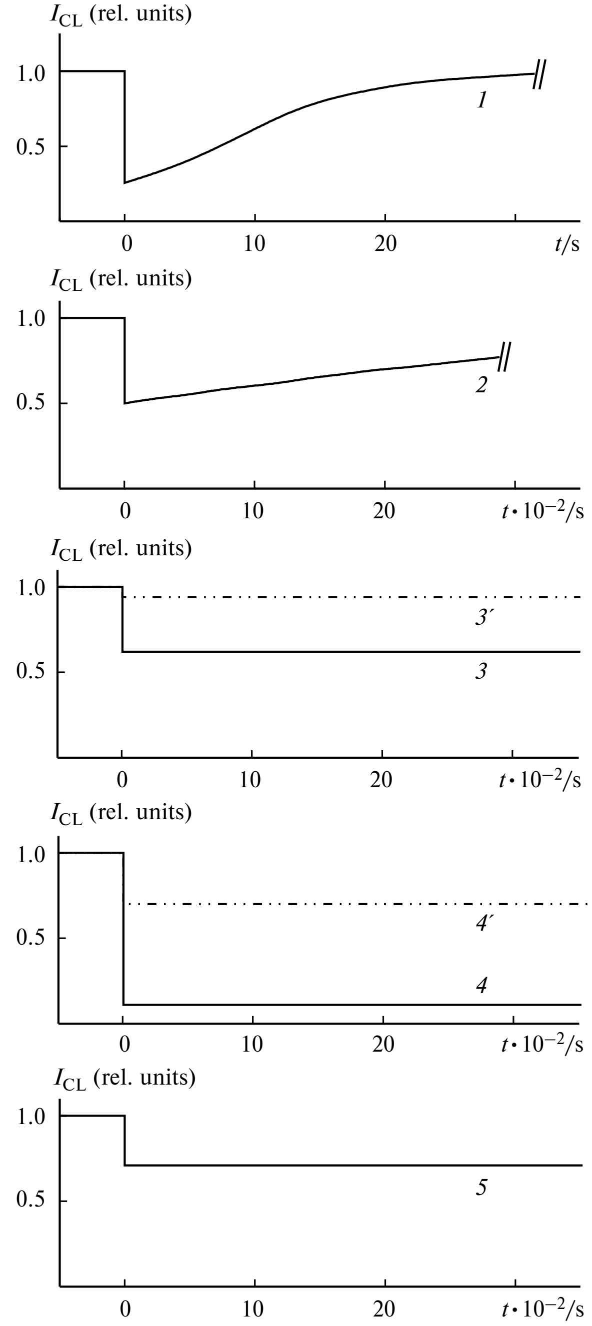


Fig. 1. Effect of fullerene C_{60} on the CL kinetics during oxidation of hydrocarbons: *1*, EB (5 mL), AIBN ($3.0 \cdot 10^{-3}$ mol L^{-1}), DBA ($5.9 \cdot 10^{-4}$ mol L^{-1}), α-tocopherol ($3.2 \cdot 10^{-7}$ mol L^{-1}), 60 °C; *2*, CH (12 mL), DCHPC ($2.1 \cdot 10^{-3}$ mol L^{-1}), DBA ($4.2 \cdot 10^{-4}$ mol L^{-1}), ionol ($2.0 \cdot 10^{-5}$ mol L^{-1}), 60 °C; *3*, *3′*, EB (5 mL), AIBN ($2.8 \cdot 10^{-3}$ mol L^{-1}), DBA ($6.8 \cdot 10^{-4}$ mol L^{-1}), $[C_{60}] = 1.5 \cdot 10^{-4}$ (*3*) and $4.8 \cdot 10^{-5}$ mol L^{-1} (*3′*), 60 °C; *4*, *4′*, DD (2.5 mL) + DCB (2.5 mL), AIBN ($4.4 \cdot 10^{-3}$ mol L^{-1}), DBA ($1.2 \cdot 10^{-3}$ mol L^{-1}), $[C_{60}] = 1.7 \cdot 10^{-3}$ (*4*) and $4.5 \cdot 10^{-4}$ mol L^{-1} (*4′*), 80 °C; *5*, OA (2.0 mL) + DCB (5.0 mL), $Eu(TTA)_3 \cdot phen$ ($2.6 \cdot 10^{-4}$ mol L^{-1}), DBA ($8.5 \cdot 10^{-4}$ mol L^{-1}), $[C_{60}] = 3.5 \cdot 10^{-4}$ mol L^{-1}, 80 °C. The moments of addition of inhibitors (*1*, *2*) or C_{60} solution (*3*, *3′*, *4*, *4′*, and *5*) are accepted as zero.

ferred from ketones to A, which are transformed into excited states A* (reaction (10)), and the latter are the secondary emitters of CL.[14,16,18] The decrease in the CL intensity is a result of the interaction of $RO_2^{\bullet}$ with inhibitor (reaction (9)). Reaction (9) competes with the generation of the CL emitters (reaction (8)). The consumption of the inhibitors in reaction (9) recovers the CL intensity.

The addition of solutions of C_{60} at the moment of hydrocarbon oxidation also induces a sharp decrease in the CL intensity. The depth of this decrease is proportional to the fullerene concentration (see Fig. 1). However, after this decrease, the CL intensity remains at a constant level, which is lower as compared to the initial value. It could be assumed that this decrease and the constant CL level are caused by a very high inhibition ability of C_{60}, which results in a prolonged consumption of C_{60} in the reaction with peroxide radicals. An argument against this assumption is the absence of a decrease in the CL intensity at lower C_{60} concentrations, or a weaker decrease is observed, after which a constant CL level is detected (see Fig. 1, dash-dot lines). According to the HPLC data, the content of C_{60} is the same immediately after addition to the reaction solution and after prolonged detection of a constant CL level. Therefore, the observed decrease in the CL intensity is not caused by the chemical interaction of fullerene with radicals and other more stable participants of hydrocarbon oxidation. At the C_{60} concentrations used, the CL decrease is caused by the effect of internal filter only to a small extent, and the latter is due to CL absorption by fullerene.

These results suggest that the decrease in the CL intensity is caused by quenching of CL emitters with fullerenes. This conclusion is confirmed by the observed ability of C_{60} to quench electron-excited states (generated upon photoexcitation) of different nature: triplet states of aldehydes and ketones, singlet states of polycyclic aromatic hydrocarbons, and excited lanthanide ions. (The obtained quantitative data on quenching of these excited states by fullerenes, which include rate constants of these processes, and quenching mechanisms will be reported elsewhere.)

Thus, based on our results, we can conclude that fullerene C_{60} does not react with peroxide radicals $RO_2^{\bullet}$ and does not inhibit hydrocarbon oxidation with oxygen.

Since hydrocarbons of different nature (alkylaromatic (EB), saturated (DD), and unsaturated (OA)) were oxidized, the nature of the corresponding radicals is also diverse. This allows us to extend the conclusion on inertness of C_{60} to radicals $RO_2^{\bullet}$ over other types of radicals. In addition, as shown earlier,[22] the rate constants of $RO_2^{\bullet}$ disproportionation depend weakly on the nature of these radicals.

Thus obtained evidence for inertness of fullerene C_{60} toward the $RO_2^{\bullet}$ radicals provides a new interpretation of published data on the kinetics of peroxide oxidation of lipids and TOD of polymers. We believe that the effect of decreasing the overall light intensity of CL during peroxide oxidation of lipids due to the addition of the polyvinylpyrrolidone complex of C_{60} is not related to the inhibition effect of C_{60} and accepting $RO_2^{\bullet}$ radicals by fullerene C_{60} but is caused by quenching of the CL emitters with fullerene. According to earlier published data,[21] the emitters of this CL are triplet-excited ketones as in our case. It is incorrect to conclude the inhibition activity of any compound from the fact of decreasing the CL intensity and ignore quenching processes. It seems improbable that fullerene inhibits TOD of polymers[7] *via* reaction (2) for the following reasons. First, if reaction (2) occurred, then the HPLC chromatograms would contain a peak of epoxide $C_{60}O$, which is easily detected[20] along with the peak of C_{60} when analyzing products of other reactions. However, when hydrocarbons are oxidized in the presence of C_{60}, the HPLC chromatograms exhibit only the peak of fullerene. Second, the $RO_2^{\bullet}$ radicals disappear due to reaction (2), and other radicals are formed: $RO^{\bullet}$. Since the rate constants of chain propagation (reaction (6)) is by several orders of magnitude higher than those for reaction (7),[23] the TOD rate should increase in the presence of C_{60} instead of inhibition

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}. \qquad (11)$$

Taking into account these facts, we assume that the inhibition of TOD of polymers is caused, most likely, by the reaction of C_{60} with radicals R_i (reaction (1)) rather than with $R_iO_2^{\bullet}$. This assumption is based on the fact that reactions of type (1) are characteristic of fullerene[2] and, according to previously published data,[7] TOD of PMMA occurs under the conditions when $[R_i] \gg [R_iO_2^{\bullet}]$.

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