Reactivity of C_{60} fullerene towards peroxy radicals generated in initiated oxidation of hydrocarbons

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At the moment the inconsistent data on ability of fullerenes to inhibit chain chemical and biochemical processes of oxidation have been accumulated. Earlier [1] chemiluminescent and volumetric methods have shown that C_{60} fullerene does not react with $RO_2^{\bullet}$ radicals generated upon oxidation of some hydrocarbons (ethyl benzene, dodecane, oleic acid). However, an attempt including application of more precision volumetry has elucidated that inhibition of the hydrocarbons liquid-phase oxidation by C_{60} takes place.

Efficiency of the fullerene effect has estimated as a degree of decrease in the initial rate of the cumene and ethyl benzene oxidation (Fig.) in the presence of C_{60}. The analysis of fullerene reactivity has performed in terms of effective rate constant of inhibition fk_{In} (f – capacity of inhibition, k_{In} – effective rate constant of the oxidation chain termination), calculated as

$$F = W_0/W_x - W_x/W_0 = fk_{In}[In]/\sqrt{2k_6W_i},$$

where [In] − concentration of inhibitor, W_0 and W_x – initial rate of the O_2 uptake in the absence and in the presence of inhibitor C_{60} respectively, F – the inhibition parameter, k_6 – the rate constant of $RO_2^{\bullet}$ bimolecular decay. As a result, $fk(C_{60})$ for inhibition of the cumene and ethyl benzene oxidation have been found to equal to $1.3\ 10^3$ and $2.0 \cdot 10^3$ L mol^{-1} s^{-1}. For comparison: fk of ionol, a typical synthetic antioxidant, measured in the same conditions equals to $2.1 \cdot 10^4$ L mol^{-1} s^{-1}.

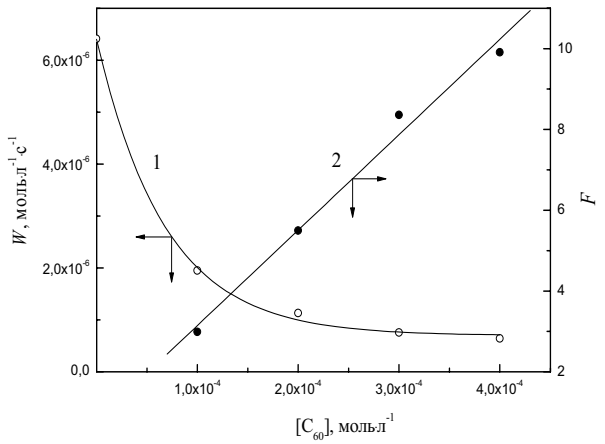

Figure Initial rate of the cumene oxidation W (1) and the inhibition parameter F (2) vs. the C_{60}concentration, T = 343 K, $W_i = 9\ 10^{-8}$ L mol^{-1} s^{-1}.

Apparently, the efficiencies of inhibition by fullerene and ionol differ by an order that allows concluding the lability fullerene radicals, i.e. the possibility of these radicals to participate not only in the chain termination processes but also in the chain initiation and propagation of radical oxidation process.