Derivatives of buckminsterfullerene as efficient inhibitors in a model hydrocarbon oxidation environment

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Abstract

The developed system of conjugated s–p bonds arranged in the fullerene molecule in a closed shape can promote a strong resonance effect on the grafted units and increase the hydrogen atom abstraction efficiency. In this case the known ability of fullerene to trap alkyl radicals might be combined with an additional antioxidant functionality to afford a new class of antioxidants with a multiple action.

This article furnishes an anti-oxidative influence of novel amine derivatives of buckminsterfullerene on the model hydrocarbon oxidation environment. The antioxidant activity of the investigated derivatives was studied by measuring the inhibition rate constants for their reaction with alkyl and peroxy radicals in a model cumene initiated (2,2'-azobisisobutyronitrile, AIBN) oxidation experiments and compared to that recorded under identical experiments for buckminsterfullerene itself and commercial primary amine stabilizers.

The results indicate that linking the amine moieties containing –NH groups directly to the fullerene core gives rise to the appearance of a new chain breaking antioxidative mode for the buckminsterfullerene while cyclic fragments containing the same but distant amine group do not reveal this ability. The inhibition rate constants for trapping of peroxy radicals by the amine derivatives were found to be higher than that of known aromatic amine antioxidants Neozone-D and Naugard 445. In addition the C_{60} part of these molecules acts synergically by trapping alkyl radicals with inhibition rate constants which exceed that of underivatized fullerene.

These novel C60–amine conjugates may be considered as promising molecules for broad-spectrum radical scavenging antioxidants to be purposely used in polymer or oil materials.

Keywords: Buckminsterfullerene ; Fulleropyrrolidine; Fulleropiperidine; Model oxidation; Rate of oxidation; Radical scavenger; Antioxidative efficiency; Inhibition rate constant.

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INTRODUCTION

Fullerenes are now widely known as effective scavengers of carbon-centered radicals [1 - 10]. They are recommended in practical end-use applications as inhibitors of chain radical polymerization and thermal stabilizers for polymer materials [2, 5, 6, 11 - 27]. However, along with this advantage there is certain limit to the use fullerenes as antioxidants because of their insusceptibility towards peroxy radicals [2, 28, 29]. In order to gain this important ability, essential for effective antioxidative functioning, fullerenes may be further modified, especially since the fullerene molecule, is essentially a fertile framework to obtain some derived molecular design with high antioxidative capacity.

So far there are only a few publications in the literature regarding the antioxidative efficiency of such fullerene derivatives. Notably this concerns the polyhydroxylated fullerene $C_{60}(OH)_{24}$ in biological systems [30 - 33]. The fullerenol has shown excellent efficiency to scavenging stable 2, 2' –diphenyl -1-picrylhydrazyl, reactive hydroxyl (OH)-O·, nitric oxide NO· radicals, superoxide anion-radicals O_2^{-}· and other reactive oxygen species [34 - 39].

The hydrogen atom donation was proved by ESR detection of the fullerenol radical $C_{60}(OH)_{23}$. In addition it was established that the interaction between a hydroxyl radical and fullerenol is also based on a radical-addition reaction of 2n (·OH) (n = 1 - 12) radicals to the remaining olefinic bonds of a fullerenol core.

Fullerene derivatives incorporating one or two 3,5 –di-tert-butyl-4-hydroxyphenyl (BHT) units were synthesized and investigated for their antioxidative activity in controlled autooxidation experiments. The results showed that grafting of the BHT structure does not qualitatively alter the thermochemistry and kinetics of its reaction with peroxy radicals but the adducts exhibit an interesting dual mode of antioxidative action [28, 40].

Oil-soluble amine derivatives of buckminsterfullerene showed more antioxidative properties than zinc dialkyldithiophosphate as described in Ref. [41].

The antioxidant assay of fullerene substituted phenylaniline was determined in DMSO/PBS buffer to be significantly more potent than the alpha-tocopherol [42].

Thus, the field of antioxidative properties of fullerene derivatives may be envisioned as a new area with a promising future outlook.

In this work we report the results of the determination of inhibition rate constants of fullerene C_{60} amine derivatives by means of a model reaction of cumene initiated oxidation. This model oxidation has repeatedly demonstrated high resolving power on the kinetic analysis of both chain-breaking antioxidants and radical scavengers.
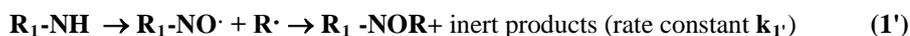
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THEORETICAL PREREQUISITES

There was clearly shown that the model oxidation relates to the onward means which effectively used for the determination of kinetic parameters of chain breaking antioxidants acting as acceptors of alkyl **R·** and/or peroxy **RO$_2$·** radicals [1, 43 - 48]. To make the determination of kinetic parameters the model reaction of cumene initiated (initiator is 2,2'- azo-bisisobutyronitrile, AIBN) oxidation was designed to proceed under steady state conditions with long kinetic chains at moderate temperatures (40 - 80ºC) where cumylhydroperoxide does not contribute additionally to the initiation of oxidation and air oxygen pressure is sufficient not to limit the process [Po$_2$ = 20 kPa ($\approx 10^{-3}$ mol O_2 l^{-1})] [49, 50].

The scheme of oxidation representing elementary stages of the antioxidants suppressing generation of free radicals [fullerene C_{60}, hindered amine stabilizer based on 2,2',6,6'-tetramethylpiperidine (HALS)] &and chain breaking antioxidants [primary phenolic or/and amine stabilizers, (InH)] has been shown to proceed according to the following mechanism:

Scheme 1*. General scheme of the model cumene initiated oxidation in the presence of the antioxidants

Chain initiation : **AIBN → r· (rO$_2$·) + RH → R·** (initiation rate is **W$_i$**)

$$\mathbf{R\cdot + C_{60} \rightarrow\ \cdot C_{60}\ R}\ \text{(rate constant }\mathbf{k_1)} \qquad \mathbf{(1)}$$

$$\mathbf{R_1\text{-}NH\ \rightarrow R_1\text{-}NO\cdot + R\cdot \rightarrow R_1\ \text{-}NOR + }\ \text{inert products (rate constant }\mathbf{k_{1'})} \qquad \mathbf{(1')}$$

Chain propagation: **R· + O$_2$ → RO$_2$·+ RH→ ROOH + R·** (rate constant **k$_2$/k$_3$**) (2)/(3)

Chain termination: **2 RO$_2$· →** inactive products (rate constant **k$_6$**) (6)

$$RO_2^{\cdot} + InH \rightarrow ROOH + In^{\cdot} \text{ (rate constant } k_7) \qquad [7]$$

$$RO_2^{\cdot} + In^{\cdot} \rightarrow \text{inactive products (rate constant } k_8) \qquad [8]$$

$$In^{\cdot} + In^{\cdot} \rightarrow \text{inactive products (rate constant } k_9) \qquad [9]$$
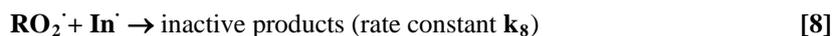
where : **RH**: cumene, **R·** : cumylalkyl radical, $RO_2^{\cdot}$: cumylperoxy radical, **ROOH** : cumylhydroperoxide) , C_{60} : buckminsterfullerene, $\cdot C_{60}$ **R** : radical adduct of buckminsterfullerene; $R_1\text{-}NH$: hindered amine stabilizer (HALS), $R_1\text{-}NO\cdot$: nitroxyl radical; **InH** : primary phenolic or amine antioxidant; **In·** : radical of the antioxidant;

_____

* Here the generally accepted oxidation stage numbering is used

A system of derived kinetic expressions fitting this scheme is as follows:

$$Wo_{2\,(C60)} = k_3\,[RO_2^{\cdot}]\,[RH] = W_{i\,(1)}^{1/2}\,k_3\,k_6^{-1/2}[RH] \qquad /1/$$

$$Wo_{2\,(HALS)} = k_3[RO_2^{\cdot}]\,[RH] = W_{i\,(1')}^{1/2}\,k_3\,k_6^{-1/2}[RH] \qquad /2/$$

$$W_{inh}o_2 = W_{i\,(AIBN)}\,k_3\,[RH]\,\{\,fn\,k_7\,[InH]\}^{-1} \qquad /3/,$$

with : $Wo_{2\,(C60)}$, $Wo_{2(HALS)}$ and $W_{inh}o_2$ **-** rates of oxidation in the presence buckminsterfullerene, sterically hindered amine and phenolic antioxidants, respectively; $W_{i\,(AIBN)}$, $W_{i\,(1)}$, $W_{i\,(1')}$ **-** initiation rates promoted by AIBN in the presence of a phenolic antioxidant, buckminsterfullerene, sterically hindered amine , respectively. **n**- number of functional groups in one molecule of the antioxidant; **f** - inhibition coefficient, representing the number of $RO_2^{\cdot}$ peroxy radicals deactivated per one functional group of the antioxidant or how many oxidation chains are terminated by one antioxidant group; **[InH]**- concentration of the phenolic antioxidant; k_3, k_6, k_7 – rate constants of the chain propagation, termination and inhibition, respectively.

$$W_{i\,(1)} = W_{i\,(AIBN)} - W_{(C60)} \quad /4/,$$

$$W_{(C60)} = k_{(1)}[R\cdot]\,[C_{60}] \quad /5/ \text{ - is the rate of interaction between fullerene and alkyl radical.}$$

$$W_{i\,(1')} = W_{i\,(AIBN)} - W_{(HALS)} \quad /6/$$

$$W_{(HALS)} = k_{(1')}\,[R\cdot][HALS(\text{-}NO\cdot)] \quad /7/ \text{ - is the rate of interaction between HALS and alkyl radical.}$$

The oxidation inhibited by **InH** proceeds with an induction period, τ. Length of induction time and inhibition rate constant k_7 are calculated according to the equations:

$$\tau = fn\,[InH]\,[W_{i\,(AIBN)}]^{-1} \qquad /8/$$

$$\Delta\,(O_2)\,/\,[RH] = -\,k_3\,\ln\,(1 - t\,/\tau\,)\,/\,k_7 \qquad /9/$$

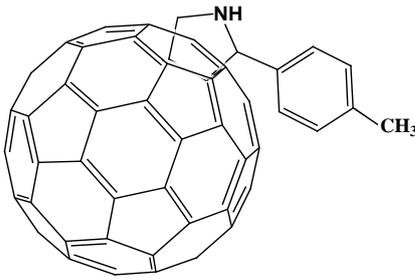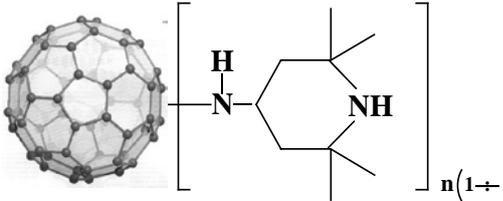with: **t -** reaction time; $\Delta(O_2)$ - volume of absorbed oxygen.

EXPERIMENTAL

Amine derivatives of buckminsterfullerene

The compounds used in this work were synthesized in the laboratory environment. The procedure of synthesis and their chemical structures are given in Table 1.

Table 1. Amine derivatives of buckminsterfullerene used in the work.

Symbolic notation/chemical name	Synthesis procedure	Chemical structures (molecular weight MW)

1. C_{60}-AmAO-1 Fullerene-4-methylphenyl-pyrrolidine	C_{60}:glycine:4-methyl-benzaldehyde = 0.07:0.14:0.35(mmol), under N_2, refluxed in toluene , purified in column chromatography	**NH** — structure with CH₃
		MW = 879
2. C_{60}-AmAO-2 Fullerene-amino-2,2',6,6'-tetra-methylpiperidine [51]	C_{60} : 4-amino-2,2',6,6'-tetramethylpiperidine = = 0.05g: excess of the amine, stirred under N_2 at room temperature in toluene. Remaining amine is distilled off, product washed with hexane.	structure $n(1 \div 6)$
		MW(average) = 1197 (n = 3)

The amine derivatives can be conditionally subdivided into two types: 1) C_{60}-AmAO-1 is fullerene derivative with grafted sterically hindered pyrrolidine fragment; 2) C_{60}-AmAO-2 is fullerene derivative with grafted sterically hindered piperidine moiety.

Model reaction of cumene initiated oxidation

To study the chain-breaking antioxidants the model cumene oxidation was undertaken at initiation rates: $W_i = 1.7 \times 10^{-8} - 6.8 \times 10^{-8}$ Ms^{-1}, temperatures: 60 and 80 ($\pm$ 0.02)°C and oxygen pressure: $Po_2 = 20$ kPa (air). The employed cumene was 98% purity («Aldrich»).

2,2'-azobisisobutyronitrile (AIBN) was used as the initiator. The volume of the reaction mixture was 10 cm^3 (25 °C). To achieve the assigned initiation rates 0.72 - 10 mg (at 60 - 80°C) of AIBN had to be added [49, 50, 52].

The rate constants of chain propagation and termination for the cumene oxidation at 60 and 80°C have the following values: $k_3 = 1.75$ and 4.05; $k_6 = 1.84 \times 10^5$ and 3.08×10^5 $M^{-1}s^{-1}$, respectively; concentration of cumene [RH] = 6.9 (60°C) and 6.76 (80°C), mol l^{-1}. The rates of oxidation were evaluated by considering the amount of oxygen consumed, which was measured volumetrically with the simple equipment as described in [43, 50]. Oxidation rates were assessed both from slopes of the kinetic curves of oxygen consumption in the case of steady rate values and also by means of differentiating the curve in the case of an observed induction period. Induction periods were graphically evaluated from kinetic curves [49, 50].

Values of the inhibition rate constant k_7 were found from the slopes of semilogarithmic transformation of oxygen absorption curves according to the relationship

$$k_7 = 2.3 \, k_3 \, [RH] \, (tg\alpha)^{-1} \quad /10/, \text{ with } tg\alpha = \Delta \, (O_2) \, [- \lg \, (1 - t \, / \tau \,)]^{-1}$$

From the experimentally observed values of oxidation rates, using the known rate constants for cumene oxidation it is possible to determine inhibition rate constants k_1 (or $k_{1'}$) for the trapping cumylalkyl radicals by the fullerene or HALS type compounds:

$$k_1[R^\cdot] \, [C_{60}] \{ k_{1'}[R^\cdot] \, [HALS]\} = W_{i \, (AIBN)} - [Wo_{2 \, (C60)}]^2 \{Wo_{2 \, (HALS)}\} \, k_6 \, (k_3)^{-2} \, [RH]^{-2} \quad /11/$$

Experiments were carried out at least in triplicate and the correctness in determining the kinetic parameters was within the range 1-10%.

RESULTS AND DISCUSSION

Kinetic study of C_{60}-AmAO-1

The compound structure is buckminsterfullerene with directly grafted pyrrolidine fragments having sterically hindered bulky phenyl substituent. Apparently such propriety head to tail structure is a good realization for the mechanism of alkyl radical scavenging. Figure 1 represents the kinetic dependences of oxygen uptake in the model oxidation reaction in the presence of C_{60}-AmAO-1.
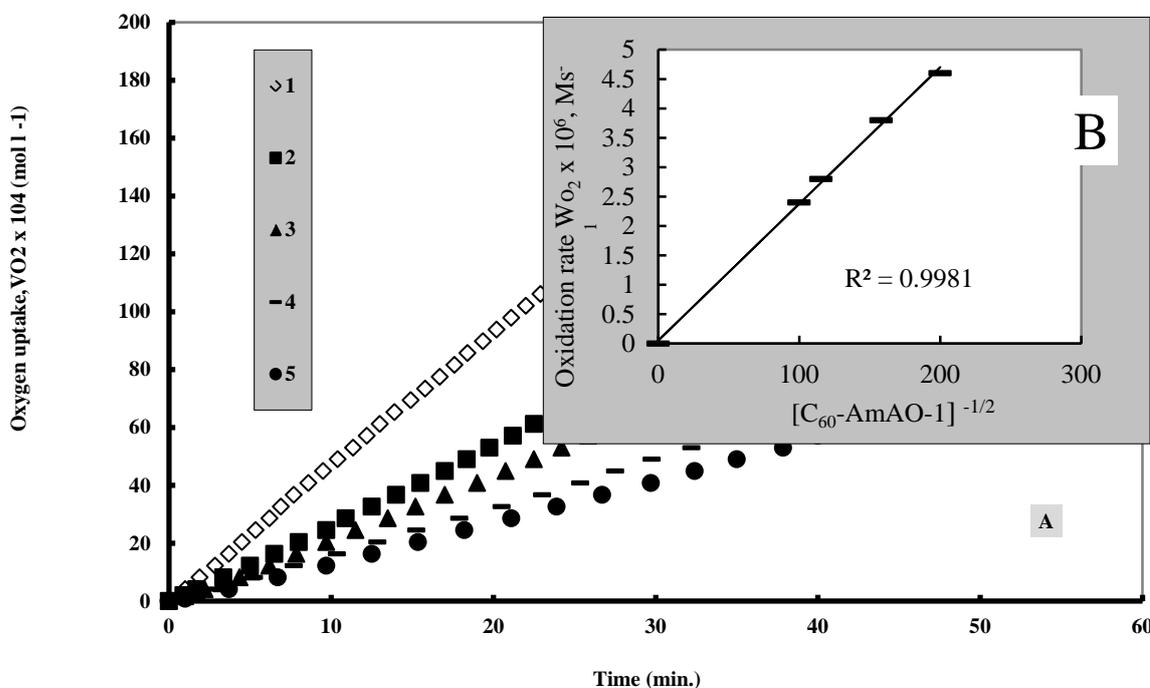

Figure 1. Kinetic dependences of oxygen oxygen-uptake (**A**) for initiated oxidation of cumene in the absence (**1**) and presence of different amounts of amine derivatives of fullerene C_{60} (**2 - 5**); **B:** is plot of induction period versus concentration of the compounds.

The initiator is 2,2′-azobisisobutyronitrile (AIBN), initiation rate:$W_i = 6.8 \times 10^{-8}$ Ms^{-1}, reaction mixture volume:10 ml, oxygen pressure:$Po_2 = 20$ kPa (air), temperature: 60^oC.

Concentration of the fullerene derivatives - $[C_{60}$-AmAO-1$]$: (**1**) = 0, (**2**) = 2.5×10^{-5}, (**3**) = 4×10^{-5}, (**4**) = 7.5×10^{-5}, (**5**) = 1.0×10^{-4}, mol/l;

It is seen from Figure 1 that over a sufficient wide range of concentrations of the added amine derivative the kinetic curves of oxygen consumption do not exhibit any induction period and the model oxidation proceeds with a retarded steady oxidation rate. Such a behaviour pattern is consistent with scheme 1 and the related Eqs**./1, 2/** and the following Eq./**12**/: $Wo_{2 \ (C60-AmAO-1)} = k_3 [RO_2 \cdot] [RH] = W_{i \ (C60-AmAO-1)}^{1/2} k_3 k_6^{-1/2}[RH]$ /**12**/ . The dependence plotted in the Figure 1(B) manifests quite a good linearity between the experimentally observed oxidation rates $Wo_{2 \ (C60-AmAO-1)}$ and the square root of the concentration of the compounds over the range $2.5 \times 10^{-5} - 1.0 \times 10^{-4}$ mol/l i.e.$Wo_{2 \ (C60-AmAO-1)} \sim [C_{60}$-AmAO-1$]^{1/2}$.

The inhibition rate constants for the C_{60}-AmAO-1 may be calculated from the following Eq. /**13**/: $k_{(C60-AmAO-1)} = 10^{6} \{ W_{i \ (AIBN)} - [Wo_{2 \ (C60-AmAO-1)}]^2 k_6 (k_3)^{-2} [RH]^{-2} \} [C_{60}$-AmAO-1$]^{-1} [Wo_{2 \ (C60-AmAO-1)}]^{-1}$ /**13**/. Values of the inhibition rate constants found for the buckminsterfullerene amine derivatives C_{60}-AmAO-1 over the concentration range $2.5 \times 10^{-5} - 1.0 \times 10^{-4}$ mol/l are given in Table 2.

Table 2. Rate constants for the addition of cumylalkyl radicals to the buckminsterfullerene, amine derivatives of buckminsterfullerene and reference alkyl radical scavenging stabilizers.

Antioxidant/stabilizer	The inhibition rate constant, $k_{(333K)}$ $M^{-1} s^{-1}$	Reference
C_{60}	$(1.9 \pm 0.2) \times 10^8$	[1]
C_{60} –AmAO-1	$(3.4 \pm 0.5) \times 10^8$	found
C_{60} –AmAO-2	$(5.1 \pm 0.6) \times 10^8$	[51]
Cyasorb 3529 (1,6-Hexanediamine, N,N'- bis (2,2,6,6-tetramethyl-4-piperidinyl)-, Polymers with morpholine-2,4,6,-trichloro-1,3,5,- triazine)	$(2.0 \pm 0.8) \times 10^8$	[46]
Chimassorb 119 (1,3,5-Triazine-2,4,6,-triamine, N,N'''-[1,2-ethane-diyl-bis [[[4,6-bis-[butyl (1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazine-2yl-]imino]-3,1-propanediyl]]bis [N',N''- dibutyl-N', N''- bis (1,2,2,6,6-pentamethyl-4-piperidinyl)	$(1.2 \pm 0.2) \times 10^8$	[45]
Chimassorb 119FL	$(1.4 \pm 0.2) \times 10^8$	[45]
Chimassorb 2020 (1,6-Hexanediamine, N, N'-bis (2,2,6,6-tetramethyl-4-piperidinyl)-polymer with 2,4,6-trichloro-1,3,5- triazine, reaction products with N-butyl-1-butanamine an N-butyl-2,2,6,6-tetramethyl-4-piperidinamine)	$(1.5 \pm 0.2) \times 10^7$	[43]

The evaluated rate constants appear to be considerably higher than those of fullerene and given commercials stabilizers, confirming the existence of a synergistic effect promoted by the fullerene component and the tethered amine units. It is possible also to infer that the more the steric hindrance in the grafted cyclic amines the higher the values of inhibition rate constants.

4.2 Kinetic analysis of C_{60}-AmAO-2

This amine derivative has an interesting structure where the sterically hindered piperidine unit which is widely known as a precursor of nitroxyl radicals is connected with secondary amine groups directly grafted to the buckminsterfullerene core. Hence, the mentioned double antioxidative capacity of the molecule due to hydrogen atom abstraction of the –NH group followed by interaction with peroxy radicals and additionally scavenging of alkyl radicals by nitroxyl radicals and the fullerene part itself might be expected.

The kinetic regularities of oxygen consumption, dependence of induction period vs C_{60} -AmAO-2 content as well as semilogarithmic patterns of the initial plots of kinetic curves are shown in the Figures 2 and 3, respectively.
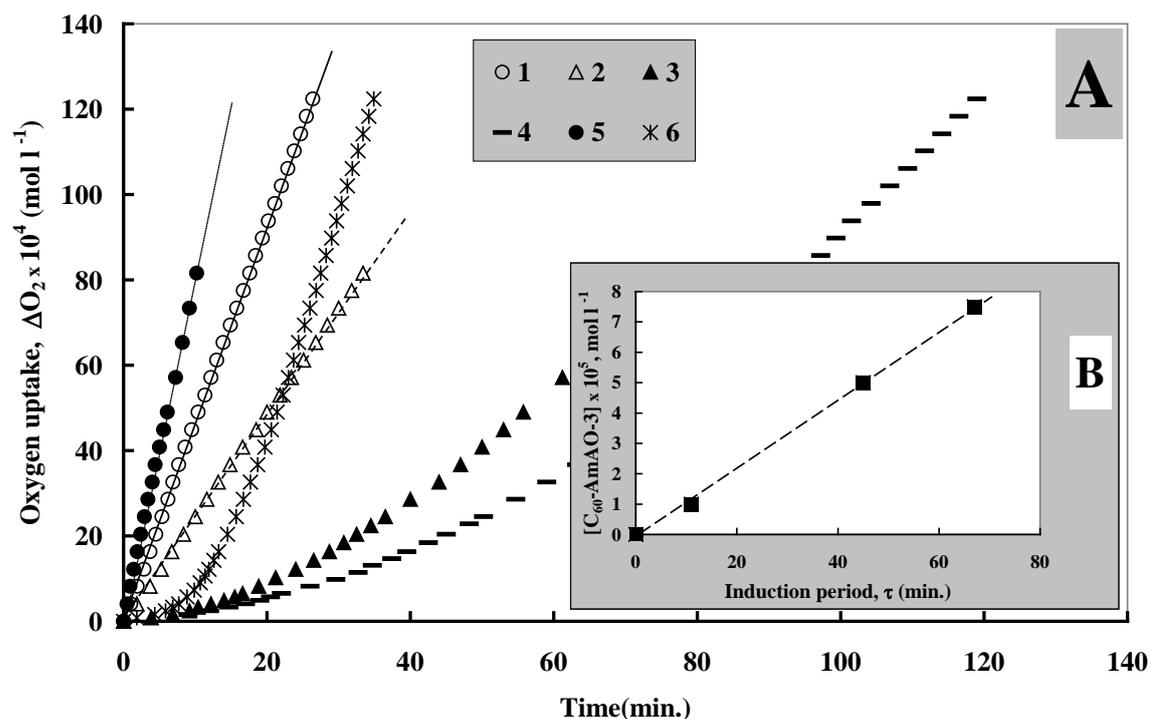
Figure 2. Kinetic dependencies of oxygen uptake (**A**) and dependence induction period vs content (**B**) for cumene initiated oxidation in the presence of buckmisterfullerene amine derivative C_{60} -AmAO-2. Initiator is 2,2'-azobisisobutyronitrile (AIBN), initiation rate:
$W_i = 6.8 \times 10^{-8}$ Ms^{-1}, reaction mixture volume:10 ml, oxygen pressure: $Po_2 = 20$ kPa (air), 60° and 80^oC.
A - **[C_{60} -AmAO-2]:** 60^oC - (**1**) 0; (**2**) 1.0×10^{-5}; (**3**) 5×10^{-5}; (**4**) 7.5×10^{-5}, mol l^{-1}; 80^oC - (**5**) 0; (**6**) 2.0×10^{-5}, mol l^{-1}.

The results of the inhibition rate constant k_7 determination for the compound C_{60} -AmAO-2 is given in Table 3.

The values of post induction oxidation rates of the kinetic curves plotted in Figure 2 are lower than that of benchmark dependency (curve1). The lowering has occurred because of the simultaneous trapping of alkyl radicals by the fullerene part of the molecule C_{60} -AmAO-2 and by the 2,2',6,6' -tetramethylpiperidine moiety of the substituent. In order to quantify the inhibition rate constant of alkyl radical scavenging the post-induction time plots of kinetic curves of oxygen consumption were arranged in Figure 4 and calculated oxidation rates were compared with that obtained for the fullerene C_{60} molecule only [1].
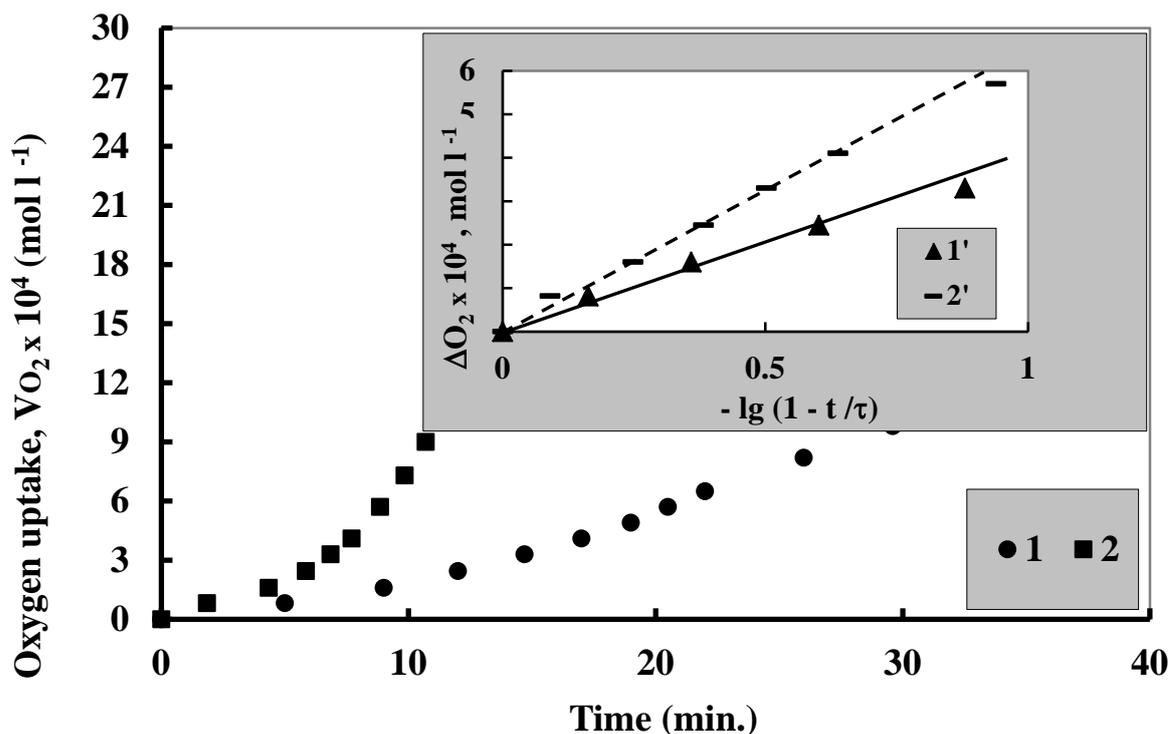
Figure 3. Initial plots of kinetic curves of oxygen uptake (**1, 2**) and their graphical anamorphoses (**1', 2'**) for cumene initiated oxidation in the presence of buckminsterfullerene amine C_{60} -AmAO-2. Reaction mixture volume: 10 ml, rate of initiation: $W_{i(AIBN)} = 6.8 \times 10^{-8}$ M s^{-1}, oxygen pressure: $Po_2 = 20$ kPa (air). **1:** [C_{60} -AmAO-2] = 7.5×10^{-5} mol/l, 60°C; **2:** [C_{60} -AmAO-2] = 2.0×10^{-5} mol/l, 80°C.
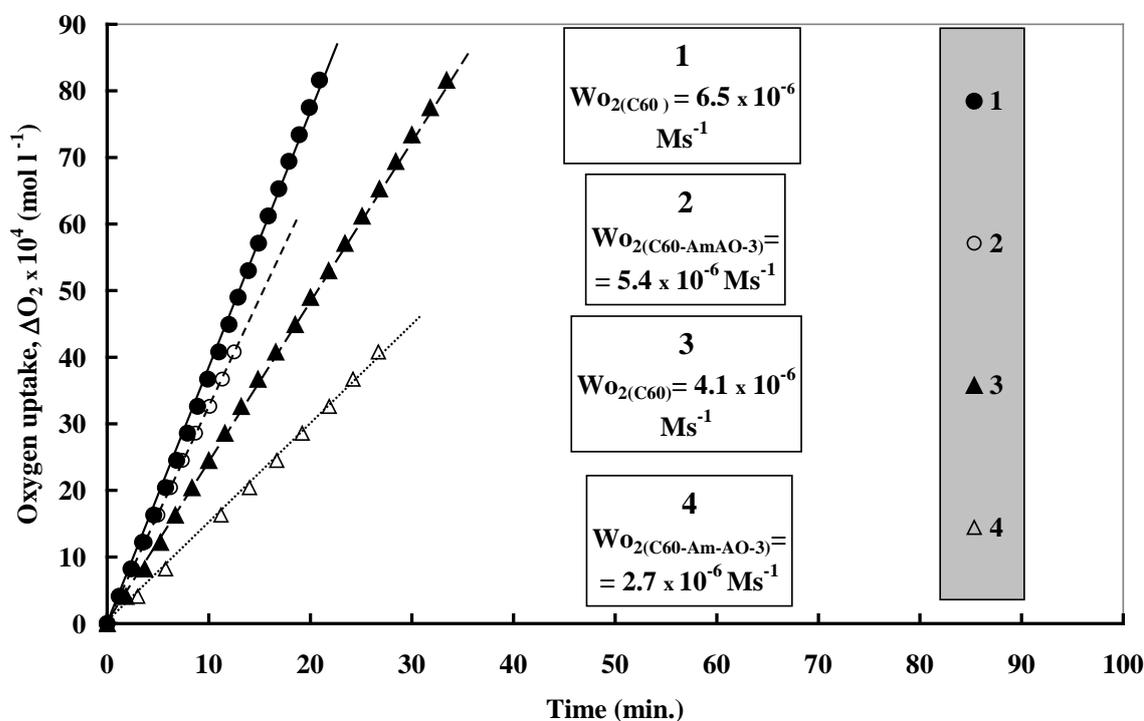

Figure 4. Kinetic lines of oxygen oxygen-uptake during aerobic initiated oxidation of cumene in the presence of buckminsterfullerene (**1, 3**) and the amine derivative C_{60} -AmAO-2 (**2, 4**; post-induction period plots are given).The initiator is 2,2′-azobisisobutyronitrile (AIBN), initiation rate:$W_i = 6.8 \times 10^{-8}$ mol/l s, reaction mixture volume10 ml, oxygen pressure:$Po_2 = 20$ kPa (air), temperature: 60°C. [C_{60}] and [C_{60} -AmAO-2] : (**1, 2**) = 1×10^{-5}, (**3, 4**) = 5×10^{-5} mol/l.

Table 3. Kinetic parameters of antioxidative activity of the amine derivative of buckminsterfullerene C_{60}-AmAO-2 and also of known primary antioxidants in the model reaction of cumene initiated oxidation. $(k_7)_0$ – pre-exponential factor, E - activation energy.

Antioxidant	lg $(k_7)_{(333K)}$ $(M^{-1}s^{-1})$	lg $(k_7)_{(353K)}$ $(M^{-1}s^{-1})$	lg $(k_7)_0$	E, kJ mol^{-1}
C_{60} -AmAO-2	4.95±0.01	5.04±0.01	6.50 ±0.40	10.1±2.5
Naugard 445, 4,4'- Bis(α,α-dimethylbenzyl) diphenylamine	4.91±0.02	5.0±0.01	6.50 ±0.50	10.1±3.4 [48]
Neozone-D, Phenyl–2-naphtylamine	4.83±0.03	4.96±0.02	7.03±0.39	14.2 ±5.9 [49]

In the earlier work [43] it was shown that the model cumene oxidation allows correct determination of antioxidants behaving as peroxy and alkyl radical scavengers simultaneously. On this basis the determination might be applicable for blends of primary antioxidants and alkyl radical scavengers, and also for one molecule which constitutes both functionalities. The presence of primary antioxidants did not counteract the determination of the alkyl radical scavengers and vice versa.

The data shown in Figure 3 shows quite a good proportionality between the experimentally observed values of oxidation rates $\mathbf{Wo_{2\,(C60)}}$ -$\mathbf{Wo_{2\,(C60\text{-}AmAO\text{-}2)}}$ and the square root of concentration (**C**) of the compounds i.e. $[\mathbf{Wo_{2\,(C60)}} - \mathbf{Wo_{2\,(C60\text{-}AmAO\text{-}2)}}] \sim [\mathbf{C}]^{1/2}$. This implies that the buckminsterfullerene and its amine derivative C_{60} -AmAO-2 actively intercept the alkyl radicals and decrease the rate of initiation and accordingly the rate of oxidation. In this case the following expressions similar to Eqs. /**1, 2, 4 - 7**/ for the oxidation, initiation and rate of C_{60} -AmAO-2 interaction with alkyl radicals are valid:

$$\mathbf{Wo_{2\,(C60\text{-}AmAO\text{-}2)}} = \mathbf{k_3\,[RO_2 \cdot]\,[RH]} = \mathbf{W_{i\,(C60\text{-}AmAO\text{-}2)}}^{1/2}\,\mathbf{k_3\,k_6}^{-1/2}\mathbf{[RH]} \qquad \textbf{/14/}$$

$$\mathbf{W_{i\,(C60\text{-}AmAO\text{-}2)}} = \mathbf{W_{i\,(AIBN)}} - \mathbf{W_{(C60\text{-}AmAO\text{-}2)}} \quad \textbf{/15/}$$

$$\mathbf{W_{(C60\text{-}AmAO\text{-}2)}} = \mathbf{k_{(C60\text{-}AmAO\text{-}2)}\,[R\cdot]\,[C_{60}\text{ -AmAO-2}]} \qquad \textbf{/16/}$$

Using the experimentally observed values of oxidation rates and known rate constants for cumene oxidation we may determine $\mathbf{W_{i\,(C60\text{-}AmAO\text{-}2)}}$ from the Eq./**14**/ and afterwards from equation Eqs. /**15**/ and /**16**/ an inhibition rate constant $\mathbf{k_{(C60\text{-}AmAO\text{-}2)}}$ for the trapping of cumylalkyl radicals by the buckminsterfullerene amine derivative:

$$\mathbf{k_{(C60\text{-}AmAO\text{-}2)}\,[R\cdot]\,[C_{60}\text{ -AmAO-2}]} = \mathbf{W_{i\,(AIBN)}} - \mathbf{[Wo_{2\,(C60\text{-}AmAO\text{-}2)}]}^2\,\mathbf{k_6\,(k_3)}^{-2}\mathbf{[RH]}^{-2} \qquad \textbf{/17/}$$

At steady state conditions of the oxidation for fairly long chains the rate of oxidation may be represented as [53, 54]:

$$\mathbf{k_2\,[R\cdot][O_2]} = \mathbf{k_3\,[RO_2 \cdot]\,[RH]} = \mathbf{Wo_{2(C60\text{-}AmAO\text{-}2)}} \qquad \textbf{/18/}$$

Using the known magnitudes of constants for cumene oxidation (see the experimental section) and assuming $\mathbf{k_2}$ $=10^9\,M^{-1}s^{-1}$ and $[O_2] = 10^{-3}\,M$ [53 - 56] the following expressions can be obtained for calculations of $\mathbf{k_{(C60\text{-}AmAO\text{-}2)}}$:

$$\mathbf{[R\cdot]} = \mathbf{Wo_{2(C60\text{-}AmAO\text{-}2)}} \diagup \mathbf{k_2\,[O_2]} = \mathbf{Wo_{2(C60\text{-}AmAO\text{-}2)}} / 10^6,$$

$$\mathbf{k_{(C60\text{-}AmAO\text{-}2)}} = 10^6 \{\,\mathbf{W_{i\,(AIBN0}} - \mathbf{[Wo_{2\,(C60\text{-}AmAO\text{-}2)}]}^2\,\mathbf{k_6\,(k_3)}^{-2}\mathbf{[RH]}^{-2}\}\,\mathbf{[C_{60}\text{ -AmAO-2]}}^{-1}\,\mathbf{[Wo_{2\,(C60\text{-}AmAO\text{-}2)}]}^{-1} \quad \textbf{/19/}$$

Rate constant value for the C_{60} -AmAO-2 calculated from Eq**. /19/** over the concentration range 1×10^{-5}- 5×10^{-5} mol/l and also that for known antioxidants acting as alkyl radical acceptors are accumulated in Table 2.

CONCLUSIONS

Results obtained in the work are evidence of the fact that the buckminsterfullerene derivatives containing the grafted amine units exhibit higher antioxidant efficiency than conventional commercial stabilizers-antioxidants. The found

values of inhibition rate constants also corroborate that the grafted amine containing groups are able to iteratively increase the inherent radical scavenging efficiency of the fullerene.

Thus the fullerene derivatives may be recognized as a new promising class of antioxidants.

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