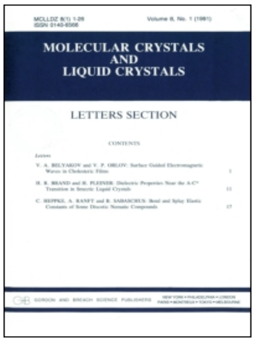
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Radical scavenging properties of piperidine derivatives of fullerene C_{60}/C_{70} and multi-walled carbon nanotubes

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ABSTRACT

Derivatives of C_{60}/C_{70} fullerene and multi-walled carbon nanotubes (MWCNTs) with piperidine fragments were synthesized and their antioxidative activity was determined. The antioxidant activity of the investigated derivatives was studied by measuring the inhibition rate constants for their reaction with peroxy radicals in a model cumene initiated oxidation experiments and compared with that for commercial primary aromatic amine stabilizers. The inhibition rate constants for trapping of peroxy radicals by the MWCNTs amine derivatives were found to be higher than that of known aromatic amine antioxidants Neozone-D and Naugard 445. These novel compounds may be considered as promising broad-spectrum radical scavenging antioxidants.

KEYWORDS

C_{60}/C_{70} fullerene; amine derivatives of carbon nanotubes; rate of model oxidation; antioxidant efficiency; inhibition rate constants

1. Introduction

Single and multi-walled carbon nanotubes (SWCNTs and MWCNTs, respectively) possess extraordinary mechanical and electronic properties [1–9]. However, manipulation and processing of NTs has been limited by their agglomeration tendency and insolubility in most common organic solvents, although some progress has recently been obtained [10–12]. Considerable efforts have therefore been made to modify the NTs chemically, electrochemically and plasmachemically, which might pave the way to many useful applications, including composite preparations [13–17]. Particularly, in order to gain the important ability to dissolve in a liquid phase, essential for effective functioning, carbon nano-compounds -fullerenes, SWCNTs and MWCNTs may be modified by different amines.

Reactions of buckminsterfullerene with allyl chloride, methallyl chloride, cinnamyl chloride, propargyl bromide, ethyl bromoacetate, bromoacetonitrile, bromomethane, bromopropane and bromobutane and amino acids to produce fulleropyrrolidines have been described in the work [18]. This reaction can be considered as alternative to the reaction for synthesizing fulleropyrrolidines where expensive or hard to reach aldehydes are used. A plausible reaction mechanism for product formation involving C-X bond cleavage in the halide to form the aldehyde is proposed.

The authors have found that the adducts of the fullerene - pentaamino hydroxyl adduct C-60(OH)$(NR_1R_2)_5$ and hexaamino adduct C-60(OH)$(NR_1R_2)_6$ can be formed as the major products in the dark under thermal exposure in the presence of oxygen [19].

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A method has been developed for synthesising a series of soluble C_{60} containing polymers which have the characteristic photo-physical properties of monosubstituted-fullerene derivatives [20]. The strategy employed required that first a suitably derivatised mono-fulleropyrrolidine was prepared and characterised which was then subsequently reacted with an acryloyl chloride functionalised polymer. The amino group of the fulleropyrrolidine reacts with the acyl chloride functional groups of the polymer forming an amide bond. This approach enabled the preparation of several soluble fullerene/acrylic polymers with a controlled and high covalently bonded fullerene content. The resulting fullerene derivatised methacrylate polymers were characterised by UV, infrared and gel permeation chromatography [20].

MWCNTs functionalized with amino groups were prepared via chemical modification of carboxyl groups introduced on the carbon nanotube surfaces [21]. Oxidation of MWCNTs was performed with ozone in aqueous phase and amidation of generated carboxylic groups was occurred with amines in the presence of HATU {N-[(Dimethylamino)-1H-1,2,3-triazolo-[4,5-b]pyridin-1-ylmethylene]-Nmethylmethanaminium hexafluorophosphateN-oxide} as a coupling agent. The functionalized MWCNTs were characterized in detail using FTIR-ATR, Raman CHN and SEM methods. Obtained functionalized MWCNTs are soluble in many common organic solvents [21]. The latter ability concerning both types of carbon nanocompounds - fullerenes and MWCNTs are preferable to gain the effective acting in liquid-phase oxidation environments. In spite of the absence of diffusion restrictions for the nano-nature compounds in liquid mediums, the agglomeration and bunching of the molecules, occurring because the higher superficial energy should also be taken into consideration [22].

This article describes the effect of both fullerene and MWCNTs piperidine derivatives on the model oxidation of cumene under a mild condition. The model oxidation environments have repeatedly demonstrated high resolving power upon the kinetic analysis of chain-breaking antioxidants and radical scavengers [23–25].

2. Experimental part

2.1. Carbon nanocompounds

Fullerenes C_{60}/C_{70} (85/15%) were provided by Xzillion GmbH & Co. KG (recently renamed to Proteome Sciences R&D GmbH & Co. KG).

Multi-walled carbon nanotubes denoted as CNT-MW manufactured by German Future-Carbon GmbH with mean diameter of particles: 10–20 nm, length −5–10 μm, BET-surface $\sim$ 200 m^2 was involved in the experiments.

2.2. Model cumene oxidation reaction

The model cumene oxidation was undertaken at initiation rates: $\mathbf{W_i} = 1.7 \times 10^{-8} - 6.8 \times 10^{-8}$ Ms^{-1}, temperatures: 60 and 80 (± 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 [26–28].

The rate constants of chain propagation for the cumene oxidation at 60 and 80°C have the following values: $\mathbf{k_3} = 1.75$ and 4.05, $M^{-1}s^{-1}$, respectively, concentration of cumene $[RH] = 6.9$ (60°C) and 6.76 (80°C), mol l^{-1}. The rates of oxidation ($\mathbf{Wo_2}$) were evaluated by

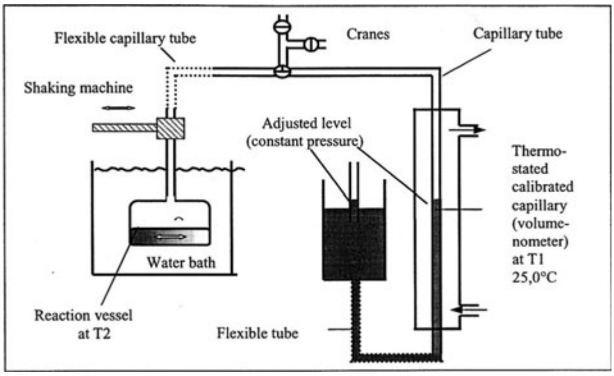

Figure 1. Schematic diagram of measuring setup for oxygen consumption at constant pressure.

considering the amount of oxygen consumed $[\Delta(O_2)]$, which was measured volumetrically with the simple equipment as described in [24, 27] and shown in the Fig. 1.

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 (τ) were graphically evaluated from kinetic curves [26, 27].

Values of the inhibition rate constant k_7 were found from the slopes of semilogarithmic transformation of oxygen absorption curves according to the relationship [24, 26, 27]:

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

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

2.3. Amine derivatives of fullerene and multi-walled carbon nanotubes (CNT-MW)

The amine compounds used in this work were synthesized in the laboratory of the Institute of Catalysis & Inorganic Chemistry (Azerbaijan National Academy of Sciences) and Dalton Research Institute (Manchester Metropolitan University, UK). The procedure of synthesis and their chemical structures are given in Table 1.

The induction periods reflect the action of the secondary amine group directly connected to the fullerene and CNT-MW cores while the underivatized compound's moiety is responsible for the lowered post-induction oxidation rates. Kinetic curves show that the action of the amine derivatives is consistent with the Scheme 1.

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

$$\textit{Chain initiation}:\ \mathbf{AIBN \rightarrow r^{\cdot}(rO_2\cdot) + RH \rightarrow R^{\cdot}}\ \text{(initiation rate is}\ \mathbf{W_i})$$

$$\mathbf{R^{\cdot} + C_{60}/C_{70}(CNT-MW) \rightarrow \cdot C_{60}/C_{70}\,(CNT-MW)-R} \qquad (1)$$

$$\mathbf{R_1 - C_9H_{18}NH \rightarrow R_1 - C_9H_{18}NO\cdot + R\cdot \rightarrow R_1 - C_9H_{18}{-}NOR}{+}\text{inert products} \qquad (1')$$

$$\textit{Chain propagation}\text{:}\ \mathbf{R\cdot + O_2 {\rightarrow} RO_{2\cdot} + RH \rightarrow ROOH + R\cdot} \qquad (2)/(3)$$

$$\textit{Chain termination}:\quad \mathbf{RO_2^{\cdot} + R_1 \rightarrow ROOH + R_1^{\cdot}} \qquad (7)$$

$$\mathbf{RO_2^{\cdot} + R_1^{\cdot}} \rightarrow \text{inactive products} \qquad (8)$$

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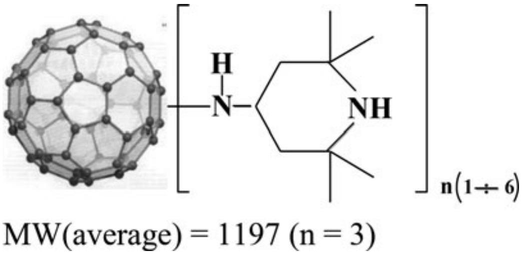
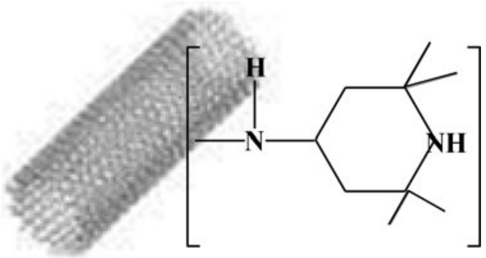
* Here the generally accepted oxidation stage numbering is used

Table 1. Features of amine derivatives of fullerenes C_{60}/C_{70} and CNT-MW used in the work.

Symbolic notation/chemical name	Synthesis procedure	Chemical structures (molecular weight MW)
1. **C_{60}/C_{70}–*Am***: Fullerene-amino -2,2′,6,6′-tetramethyl-piperidine	C_{60}/C_{70}: 4-amino-2,2′,6,6′-tetramethylpiperidine = 0.05 g: excess of the amine, stirred under N_2 at room temperature in toluene. Remaining amine is distilled off, product washed with hexane.	
2. **CNT-MW-*Am*** Multi-walled carbon nanotubes-amino-2,2′,6,6′-tetramethyl-piperidine	CNT-MW: 4-amino-2,2′,6,6′-tetramethylpiperidine = 0.05 g:excess of the amine, stirred under N_2 at room temperature in toluene. Remaining amine is distilled off, product washed with hexane.	

$$\mathbf{R_1^{\cdot}} + \mathbf{R_1^{\cdot}} \rightarrow \text{inactive products} \qquad (9)$$

where: **RH** = cumene, **R**˙ and $\mathbf{RO_2^{\cdot}}$ = cumylalkyl and cumylperoxy radicals, respectively, **ROOH** = cumylhydroperoxide, $^{\cdot}\mathbf{C_{60}/C_{70}}$ **(CNT-MW)** = carbon nanocompounds, $\mathbf{C_{60}/C_{70}}$ **(CNT-MW)-R** = radical adducts, $\mathbf{R_1}$ = C_{60}/C_{70} (CNT-MW)-NH-, $\mathbf{R_1^{\cdot}}$ = C_{60}/C_{70} (CNT-MW)-N˙-, $\mathbf{R_1\text{-}C_9H_{18}NO^{\cdot}}$ = nitroxyl radical.

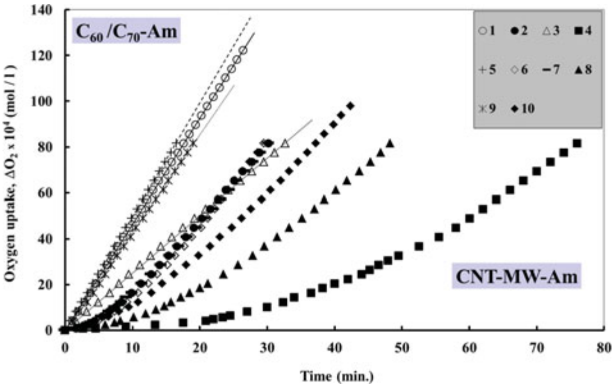


Figure 2. Kinetic dependencies of oxygen uptake for cumene initiated oxidation in the presence of C_{60}/C_{70} –Am (1–6) and CNT-MW –Am (7–10). Initiator is 2,2′-azobisisobutyronitrile (AIBN). Reaction mixture volume 10 ml, amounts of C_{60}/C_{70} –Am = 1g/l and CNT-MW –Am = 3g/l, oxygen pressure: Po_2 = 20 kPa (air), 60° and 80°C. C_{60}/C_{70} –Am **=** 1g/l: 60°C - (**1**) 0 ($W_i = 6.8 \times 10^{-8}$ Ms^{-1}); (**2**) + $W_i = 6.8 \times 10^{-8}$ Ms^{-1}; (**3**)0 ($W_i = 1.7 \times 10^{-8}$ Ms^{-1}); (**4**) + $W_i = 1.7 \times 10^{-8}$ Ms^{-1}; 80°C - (**5**) 0 ($W_i = 2.7 \times 10^{-8}$ Ms^{-1}); (**6**) + $W_i = 2.7 \times 10^{-8}$ Ms^{-1}; CNT-MW–Am **=** 3g/l: 60°C - (**7**) + $W_i = 6.8 \times 10^{-8}$ Ms^{-1}; (**8**) + $W_i = 1.7 \times 10^{-8}$ Ms^{-1}; 80°C - (**9**) 0 ($W_i = 2.0 \times 10^{-8}$ Ms^{-1}); (**10**) + $W_i = 2.0 \times 10^{-8}$ Ms^{-1}.

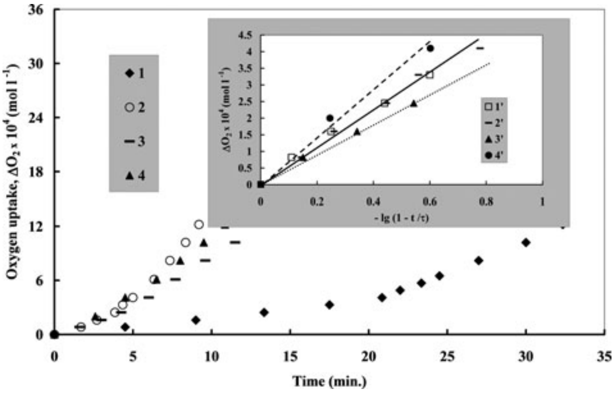


Figure 3. Semilogarithmic transformations of the initial plots of kinetic curves of oxygen consumption for cumene initiated oxidation in the presence of C_{60}/C_{70} fullerene and CNT-MW amine derivatives. Reaction mixture volume 10 ml, oxygen pressure $Po_2 = 20$ kPa (air), 60° and 80°C. C_{60}/C_{70}–Am = 1g/l: 60°C - (**1**) + $W_i = 1.7 \times 10^{-8}$ Ms^{-1} and corresponding anamorphosis (**1′**); 80°C - (**2**) + $W_i = 2.7 \times 10^{-8}$ Ms^{-1} with anamorphosis (**2′**). CNT-MW–Am = 5g/l: 60°C - (**3**) + $W_i = 1.7 \times 10^{-8}$ Ms^{-1}; CNT-MW–Am = 3g/l**:** 80°C - (**4**)+ $W_i = 2.0 \times 10^{-8}$ Ms^{-1} and their anamorphoses (**3′**) and (**4′**), respectively.

Table 2. Kinetic parameters of antioxidative activity of the C_{60}/C_{70} fullerene and CNT-MW amine derivatives and reference C_{60} fullerene amine derivatives [29] and commercial antioxidants in the model reaction of cumene initiated oxidation. Amount of C_{60}/C_{70}–Am = 10 mg, CNT-MW–Am = 3g/l, $W_i = (1.7 - 2.7) \times 10^8$ Ms^{-1}, oxygen pressure $Po_2 = 20$ kPa (air), 60° and 80°C, E - activation energy.

Antioxidant	lg $(k_7)_{(333K)}$ (M^{-1}s^{-1})	lg $(k_7)_{(353K)}$ (M^{-1}s^{-1})	E, kJ mol^{-1}
C_{60}/C_{70}–Am	5.0 ± 0.01	5.08 ± 0.02	10.2 ± 2.4
CNT-MW–Am	5.02 ± 0.01	5.12 ± 0.02	12.4 ± 2.0
C_{60}-alkylmethylene -diamines [29]	4.96 ± 0.01	5.06 ± 0.01	12.0 ± 2.0
Naugard 445, 4,4′- Bis(α,α-dimethyl benzyl)diphenylamine [23]	4.91 ± 0.02	5.0 ± 0.01	10.1 ± 3.4
Neozone-D, Phenyl–2-naphtylamine [24]	4.83 ± 0.03	4.96 ± 0.02	14.2 ± 5.9

In order to determine inhibition rate constants for the functional amine groups of the C_{60}/C_{70} (CNT-MW)-NH- moiety semi-logarithmic transformations of the initial plots of kinetic curves 4, 6, 8 and 10 (Fig. 2) are presented in Fig. 3.

Inhibition rate constants obtained from the anamorphoses and calculated according to the Eq. /1/ are presented in Table 2.

Thus, the values of inhibition rate constants for interaction of the amine derivatives of C_{60}/C_{70} fullerene and CNT-MW with cumylperoxy radicals, shown in Table 1, exceed the same constants for the known commercial primary antioxidants. The explanation for this unexpected ability should be the attached amine groups that increase the electron density of the delocalized system of the carbon compounds π-bonds that serve easier hydrogen atom abstraction from the directly grafted - NH group and leads to higher values of inhibition rate constants.

3. Conclusions

The results obtained in this work have shown that the C_{60}/C_{70} fullerene and CNT-MW derivatives containing grafted antioxidative units exhibit a higher efficiency than commercial antioxidants. The carbon nanocompound's core system of conjugated $\sigma - \pi$ bonds gives rise to a strong resonance effect with grafted amine groups and entails an instantaneous detachment of a hydrogen atom to exert strong antioxidative effect. The found values of inhibition rate constants of the cumene model oxidation also corroborate that the grafted sterically hindered piperidine moieties are able to iteratively increase the inherent radical scavenging efficiency of the carbon nanocompounds.

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