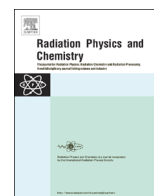




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journal homepage: www.elsevier.com/locate/radphyschemRate constants of highly hydroxylated fullerene C₆₀ interacting with hydroxyl radicals and hydrated electrons. Pulse radiolysis studyJacek Grebowski^a, Anita Krokosz^{a,*}, Anna Konarska^b, Marian Wolszczak^b, Mieczyslaw Puchala^a^a Department of Molecular Biophysics, Faculty of Biology and Environmental Protection, University of Lodz, 141/143 Pomorska Street, 90-236 Lodz, Poland^b Institute of Applied Radiation Chemistry, Technical University of Lodz, 15 Wroblewskiego Street, 93-590 Lodz, Poland

HIGHLIGHTS

- The rate constants of the reaction of fullereneol with $\bullet\text{OH}$ or e_{aq}^- were determined.
- The rate constant for the reaction of C₆₀(OH)₃₆ with $\bullet\text{OH}$ is $2.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
- The rate constant for the reaction of C₆₀(OH)₃₆ with e_{aq}^- is $2.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
- The reaction of $\bullet\text{OH}$ with fullereneol was *via* the formation of a π -complex.

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ABSTRACT

Pulse radiolysis was applied to investigate the reaction of C₆₀(OH)₃₆ with $\bullet\text{OH}$ radicals or hydrated electrons (e_{aq}^-). The second-order rate constants for the reactions between fullereneol and $\bullet\text{OH}$ radicals ($2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) or hydrated electrons ($2.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) were determined. The most probable mechanism of the reaction of $\bullet\text{OH}$ with fullereneol was *via* the formation of a π -complex that could dissociate to reform the reactants in competition with the rearrangement to the σ -complex. The large number of hydroxyl groups attached to the fullereneol carbon cage did not result in any significant change in the rate constant for the reaction of fullereneol with hydroxyl radicals or e_{aq}^- .

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1. Introduction

In recent years, considerable attention has been paid to the properties of bioactive water-soluble fullerene derivatives, with special regard to their ability to generate and scavenge reactive oxygen species (ROS) and reactive nitrogen species (RNS) (Vileno et al., 2010; Lao et al., 2009). The idea of using fullerenes to protect cells against ROS/RNS is connected to the chemical and biological properties of fullerenes and their derivatives (Grebowski et al., 2013a). Fullerenes are often considered effective scavengers of free radicals based on the fact that they have a large number of conjugated π bonds and a Lowest Unoccupied Molecular Orbital (LUMO) with low energy, which can easily accept an electron. For these reasons, fullerenes are very vulnerable to attack by radicals (Krusic et al., 1991) and due to their ability to react with free radicals, are regarded as “radical sponges” (Xiao et al., 2006).

Commonly used free radical scavengers are water soluble C₆₀ derivatives such as PEG-C₆₀, PVP-C₆₀ and C₆₀(OH)_n (fullerenols) (Krokosz et al., 2014). Fullerenols meet all the conditions required of good radioprotectants due to the presence of double bonds (C=C), high electron affinity, ease of radical attachment, reactivity towards nucleophilic substituents and polarity of the molecule (Grebowski et al., 2013a). The radioprotective activity of fullerenols has been confirmed in *in vitro* studies conducted on human acute myeloid leukemia K562 cells (Icević et al., 2007) and fullereneol C₆₀(OH)_x inhibits radiation inactivation of antioxidant barrier enzymes such as superoxide dismutase (SOD) and glutathione peroxidase (GPx) (Bogdanović et al., 2008).

A review of literature from recent years shows the interest in highly hydroxylated fullerenes (containing 30 or more OH groups) due to their potential antioxidant properties (Saitoh et al., 2011, 2012; Inui et al., 2012). Fullereneol C₆₀(OH)₃₂·8H₂O has a protective effect on the potent membrane antioxidant β -carotene in the β -carotene bleaching assay and the authors suggest that C₆₀(OH)₃₂·8H₂O scavenges $\bullet\text{OH}$ radicals by dehydrogenation of C₆₀(OH)₃₂·8H₂O and is simultaneously oxidized to a stable radical species which may be a dehydrogenated fullereneol radical C₆₀–O \bullet (Kato

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et al. 2009). Attachment of hydroxyl groups to the surface of the carbon cage significantly changes the biological and physicochemical properties of fullerene. In all cases, even if we can assess the sizable outward, inward, and lateral displacements of the C atoms leading to the formation of highly distorted structures, no C–C bond cleavage occurs, a result that clearly demonstrates the considerable strain and flexibility that can be supported by the C₆₀ cage (Guirado-López and Rincón, 2006).

Pulse radiolysis is one of the techniques used to determine the radical reaction rate constants for both reactive oxygen and nitrogen species (Samuni et al., 2012; Goldstein 2011; Houée-Levin and Bobrowski, 2013). According to Guldi and Asmus (1999), the rate constant of the reaction between fullereneol C₆₀(OH)₁₈ and a •OH radical is $2.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. These authors propose that •OH scavenging by C₆₀(OH)₁₈ occurs in accordance with the reaction $\bullet\text{OH} + \text{C}_{60}(\text{OH})_{18} \rightarrow \text{HO}-\text{C}_{60}(\text{OH})_{18}$, which involves carbon atoms of the fullerene cage forming double π bonds. Assuming that the number of π bonds in the fullereneol molecule decrease with the subsequent attachment of hydroxyl groups, it can be expected that the reactivity with water radiolysis products will depend on the degree of fullereneol hydroxylation. However, it is not yet clear whether attachment of over 20 OH groups to C₆₀ can affect the reaction rate constant between a highly hydroxylated C₆₀ and hydroxyl radicals (•OH) or hydrated electrons (e_{aq}⁻).

Therefore, the aim of this study was to determine the rate constants of C₆₀(OH)₃₆ interacting with hydroxyl radicals (•OH) and hydrated electrons (e_{aq}⁻), the main products of water radiolysis. Knowledge of these reaction rate constants is of great importance when it comes to the use of fullereneols as potential antioxidants in different biological systems.

2. Experimental section

2.1. Chemicals

Fullerene (99.5%) was purchased from SES Research (Houston, TX, USA) and Amberlite MB20 was purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium hydroxide, hydrogen peroxide and other chemicals were purchased from POCh (Gliwice, Poland). All solutions were made with deionized water purified by the Milli-Q system.

2.2. Synthesis of fullereneol C₆₀(OH)₃₆

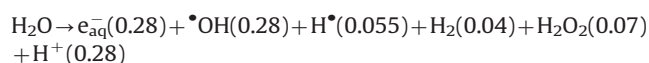
Polyhydroxyfullerene (fullereneol) C₆₀(OH)₃₆ was synthesized as previously described though the reaction time between fullerene, sodium hydroxide and hydrogen peroxide (NaOH, H₂O₂) was extended to 25 min with stirring (Grebowski et al., 2013b). An additional incubation in a 60 °C water-bath was carried out for 20 min and hydrolysis with deionized water was extended from 10 min to 24 h. After precipitation of fullereneol with methanol and resolubilization in deionized water, traces of NaOH were removed by ion-exchange chromatography using Amberlit MB-20. The structure of the hydroxylated C₆₀ fullerene derivative was confirmed by IR spectrophotometry (NEXUS FT-IR spectrometer), ¹H-NMR (Varian Gemini 200 MHz), ¹³C-NMR (Bruker Avance III600 MHz) and mass spectrometry MS-ESI (Varian 500 MS).

2.3. Pulse radiolysis measurements

Fullereneol solutions at $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ in deionized water (Millipore Milli-Q Plus system) were prepared immediately before use. Experiments were carried out at ambient temperature ($22 \pm 2 \text{ }^\circ\text{C}$). Some measurements were made for the temperature range 15–60 °C. The quartz cell containing the prepared solution

was thermostated for 15 min and then irradiated. Up to 50 °C the uncertainty in the temperature was 0.1 °C; above 50 °C the temperature of the solution might be lower than recorded by at most 0.5 °C. The equipment for pulse radiolysis in a single pulse mode with optical detection (Xe lamp 150 W) has been described elsewhere (Marszalek et al., 2013). Pulse radiolysis was performed using a 6 MeV linear accelerator and 17 ns electron pulses which delivered doses of 65 Gy each. Such samples were also used for the steady-state absorption measurements after irradiation with increasing number of pulses. Some experiments were performed with 17 ns electron pulses which delivered doses of 12 Gy each, as indicated.

UV/Vis absorption spectra were acquired using a Cary 5E (Varian) spectrophotometer. The radiolysis of water produced three well-characterized reactive radical species (e_{aq}⁻, •OH, H•), as well as molecular products (H₂O₂, H₂). Radiation chemical yields of water radiolysis products in μM per absorbed dose of 1 Gy are given in parentheses (see below) (Anderson et al., 2008).



To investigate the reaction of fullereneol with hydroxyl radicals, aqueous solutions were saturated with N₂O to convert e_{aq}⁻ into hydroxyl radicals (reaction (1), $k_1 = 8.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and to remove oxygen (Neta et al., 1988).



While studying the reactivity of hydrated electrons (e_{aq}⁻), •OH radicals could be selectively removed by 0.1 M t-butanol added to the deaerated aqueous solution (reaction (2), $k_2 = 6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) (Neta et al., 1988).



3. Results and discussion

3.1. Reaction of •OH with highly hydroxylated fullerene C₆₀

The reactions of •OH radicals have been extensively studied in aqueous solutions where they can undergo a variety of processes such as abstraction, addition and electron transfer. The hydroxyl radical reacts at diffusion-controlled rates with virtually any molecule found in its path, including macromolecules such as DNA, membrane lipids, proteins, and carbohydrates, making it a very dangerous compound to the organism (Szweda-Lewandowska et al., 2003). In this work, the reaction of •OH radicals with fullereneol C₆₀(OH)₃₆ in an aqueous solution was studied by pulse radiolysis over the temperature range 15–60 °C and steady state radiolysis at ambient temperature. Fig. 1 shows the transient absorption spectra recorded after electron pulse irradiation of N₂O-saturated aqueous solutions containing fullereneol C₆₀(OH)₃₆ at $1.5 \times 10^{-4} \text{ mol dm}^{-3}$.

The spectrum recorded at the early stage of radiolysis (0.3 μs after a 17 ns pulse irradiation at a dose of 65 Gy) was dominated by a strong absorption band in the UV region at $\sim 250 \text{ nm}$. The bleaching in the range of 230–340 nm was due to depletion of the fullereneol ground state which absorbed in this spectral region. The gradual bleaching of the UV absorption band during irradiation was accompanied by the appearance of a new absorbance band above 340 nm. A similar broad band has been observed by Guldi and Asmus (1999) in pulse radiolysis studies and attributed to the OH-adduct of C₆₀(OH)₁₈.

The transient traces showed that the evolution of absorption at 300 and 440 nm can be described by the same order kinetic

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