

Photo-Oxidation of Hydrogenated Fullerene (Fullerane) in Water

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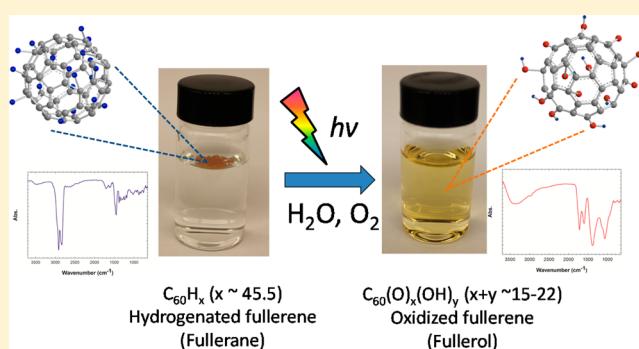
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S Supporting Information

ABSTRACT: Hydrogenated fullerenes (termed fulleranes) have been demonstrated to be key material components in advanced hydrogen storage and lithium battery technologies, among other applications; however, their potential environmental reactivity has not been evaluated to date. Here, for the first time, photoinduced oxidation and corresponding dissolution of solid fulleranes ($C_{60}H_x$, where $x = 39.9\text{--}45.5$) into water are demonstrated to occur rapidly under attenuated sunlight, UV-A irradiation, and even dark conditions, albeit more slowly as long as oxygen is present. Through a series of batch experiments, reaction kinetics demonstrate that both light and oxygen play critical roles in the solvation process as reaction rates were a function of both irradiation intensity and wavelength along with dissolved oxygen concentration. Resulting products, which were characterized by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, ultraviolet–visible spectroscopy, total organic carbon analysis, and dynamic light scattering, showed significant loss of hydrogenation and extensive oxygen-based functional group addition(s). Hydroxyl radical was identified as one of the major reactive oxygen species involved in the reaction. The increased hydrophilicity of product materials was quantified through classic octanol–water partition experiments (K_{ow}).



INTRODUCTION

Since their discovery and subsequent mass production, carbon fullerenes have been derivatized and modified for a variety of diverse applications.^{1–7} Among them, fullerene reduction via hydrogenation is recognized as a promising process for reversible hydrogen storage (through stable hydrogenation–dehydrogenation cycling).^{6,8,9} Hydrogenated fullerenes, also termed “fulleranes”,⁷ have been also used in lithium ion batteries for enhanced efficiency and extended lifetimes.¹⁰ The first fullerene hydrogenation protocol was developed by Haufler et al. through a Birch–Hückel reduction, resulting in $C_{60}H_{18}$ – $C_{60}H_{36}$ as major products.¹¹ Higher levels of C_{60} hydrogenation, with up to 50 hydrogen atoms per molecule, have been achieved via 5% Ru/carbon catalyst under high hydrogen pressures (12 MPa).¹² Relatively fast fullerene reduction with Zn and concentrated HCl (12 M) in a toluene/benzene solution has also been demonstrated, resulting in a $C_{60}H_{36}$ product.¹³ Lower levels of fullerene hydrogenation (oligohydrofullerene, $C_{60}H_x$, where $x = 2\text{--}12$) have been demonstrated via reduction by a number of metals (e.g., Cu and Zn) and even by organic reducing agents.^{14,15}

With commercial production and application, the potential for these and other fullerene materials to enter natural systems increases. Upon environmental exposure, associated reaction

pathways with (ubiquitous) reactants such as oxygen are critical to elucidate, as the identification of stable daughter products, if any, is key for accurate life cycle and risk assessments. This fact is highlighted by recent observations of facile fullerene transformation to oxidized, water-soluble products (termed fullerols) upon exposure to water, oxygen, and light.^{16,17} Compared with that of parent fullerenes, previous studies have shown the generation of reactive oxygen species (ROS) through fullerol-photocatalyzed reactions was more efficient and suggested ROS as a potential causative agent for inactivation of cells.^{16,18–21} Further, published evaluations of potential fullerene environmental implications are few. Lovren et al. evaluated the toxicity of fullerane using *Daphnia magna* as a biological receptor and reported physiological changes upon exposure, including reproductive decline.²² A major limitation of such studies is extremely low aqueous fullerene solubilities.^{23–25} To date, there is no literature report regarding the measured or estimated aqueous solubility of hydrogenated fullerenes.

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On the basis of the increasing electronegativity of fullerene carbon atoms bound to hydrogen, fullerenes should be more susceptible to electrophilic addition (i.e., oxidation) than parent fullerenes. Such reactions have been demonstrated and include oxidation of fullerenes (dissolved in *n*-hexane) under UV irradiation (254 nm)²⁶ and oxidation of C₆₀H₃₆ (dissolved in toluene open to the atmosphere) during exposure (48 h) to ambient light.¹³ To date, however, potential reactions of fullerenes directly in water have not been identified or evaluated. Herein, this work describes the oxidation and molecular solvation of solid fullerene in contact with water, which is significantly enhanced in the presence of light. Reaction kinetics of product dissolution, due to carbon cage oxidation, were examined through UV–vis spectroscopy and total organic carbon (TOC) analyses over a range of conditions, including varied photoirradiation and dissolved oxygen levels. Water-soluble, oxidized products were identified and characterized via Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Product behavior and aqueous (physical) status were further characterized with traditional octanol–water partition experiments and dynamic light scattering (DLS) analyses.

MATERIALS AND METHODS

Solid fullerenes (C₆₀H_{*x*}, where *x* ~ 45.5 and *x* ~ 39.9, averaged) were purchased from MER Corp. (Tucson, AZ), where they were prepared through direct hydrogenation in a high-isostatic pressure reactor with a hydrogen atmosphere at elevated temperatures. As received, parent fullerene materials were stored in a vacuum desiccator to avoid transformation by humidity and/or oxidation. Starting materials as received (C₆₀H_{*x*}, where *x* ~ 45.5 on average) were characterized via FTIR and XPS, shown in Figures 2a and 3a, indicating high purity, which has also been reported elsewhere.^{27,28} Solvation experiments were conducted as batch reactions with 40 mg/L solid fullerene (C₆₀H_{*x*}, where *x* ~ 45.5 on average) mixed via magnetic stirring (500 rpm) in 50 mL of ultrapure water (18.2 Ω) in customized quartz reactors (Technical Glass Products) under varied photoirradiation scenarios. Experiments conducted with attenuated sunlight (A-sunlight, filtered by borosilicate glass windows) were carried out next to a lab window (St. Louis, MO, 90°18'W, 38°38'N, July 21 to August 06, 2012). Light intensities were monitored daily with a radiometer (UVP, Inc.) and are summarized in Figure S1 of the Supporting Information. Reactions performed under monochromatic UV-A irradiation were conducted in a customized photoreactor, with fans on each side for heat dissipation, between two circuitous, monochromatic UV-A lamps (BHK Inc.) at a wavelength of 351 nm. The light intensity was calibrated as 2000 ± 50 μW/cm² by the radiometer before the reaction and corrected regularly during the reaction as needed. To delineate the role, if any, of hydroxyl radicals during the reaction(s), 10 mM *t*-BuOH was used as a hydroxyl radical scavenger.²⁹ Dark control experiments, with samples wrapped in aluminum foil, were conducted in parallel. For anaerobic conditions, solutions (50 mL) were bubbled with N₂ gas (Airgas, Bowling Green, KY) for at least 1 h to lower the dissolved oxygen concentration below 1 ppm, as tested with a microprobe DO meter (Neofox system, Oceanoptics). Anaerobic conditions were maintained via Teflon crimp-sealed caps (Wheaton Industries Inc.) and sparged with N₂ gas for 10 mins after every sampling event, leaving the sealed reactor under a slightly positive pressure. All experiments were

performed in triplicate at room temperature (21.0 ± 1.0 °C). Additional reaction and characterization details, including UV–vis, TOC, DLS, FTIR, XPS, and octanol–water partitioning observations, are included in the Supporting Information.

RESULTS AND DISCUSSION

As solid fullerene reacted in water, the observed (aqueous) product UV–vis spectra exhibited a single significant absorbance peak centered at ~210 nm [reaction for 7 days, UV-A aerobic conditions (Figure S2 of the Supporting Information)], which is consistent with the report describing the photo-oxidation (and consequent solubilization) of fullerenes to fullerols in water.¹⁷ Under direct monochromatic UV-A (351 nm wavelength) irradiation in the presence of dissolved oxygen (under open, atmospheric headspace conditions), the UV–vis absorbance (primarily in the UV region of the product spectrum) of dissolved products increases significantly as the reaction proceeds (Figure 1b and Figure S2 of the Supporting Information), consistent with the increasingly (transparent) yellow hue of the solution (Figure 1a). Additionally, the absorption peak centers of the products under UV-A irradiation shifted to longer wavelengths (from 203 to 212 nm) as the reaction continued from 1 day to 12 days, which is shown in Figure S3 of the Supporting Information. Cataldo et al. also observed such shifts during the photolysis of fullerene in *n*-hexane (maximal peak shifted from 217 to 220 nm after photoirradiation at 254 nm for 360 s). The phenomenon is hypothesized to be an artifact of sp³-hybridized carbons (hydrogenated carbon), which are predominant in the parent fullerenes, transforming back to sp²-hybridized carbon upon dehydrogenation.³⁰ For comparison, under UV-A aerobic conditions, fullerene starting material with a slightly lower number of hydrogens per molecule (C₆₀H_{*x*}, where *x* ~ 45.5 vs *x* ~ 39.9) was also evaluated (Figure 1b). While the sample exhibited a similar initial reaction rate, a lower final peak absorbance value was observed, which may result from an overall lower oxidation (product) status and/or due to different (lower) product extinction coefficient(s). Compared with that under UV-A irradiation, the increase in product absorbance under attenuated sunlight irradiation was significantly slower as the absorbance of the sunlight products after reaction for 3 days is ~19% compared to that under UV-A irradiation conditions over the same period of time. Fullerene solvation was also observed in dark experiments in the presence of dissolved oxygen, as indicated by a low-level appearance of product peaks over the described reaction time, which were the slowest rates observed. In contrast, under anaerobic conditions (dissolved oxygen content of <1 ppm), for both light and dark conditions, no apparent product peaks occurred over the same reaction times. The maximal UV absorption values at a specific wavelength (peak center) under different experimental conditions are compared in Figure 1b. Further, in the presence of 10 mM *t*-BuOH, which is a hydroxyl radical scavenger,²⁹ a significantly slower reaction rate was observed (Figure 1b) under UV-A/aerobic conditions, suggesting the involvement of hydroxyl radical in the reaction. It is hypothesized that hydroxyl radicals could be formed as secondary ROS after initial reactive oxygen species (e.g., singlet oxygen and superoxide) are produced (via fullerene intermediates) as observed by others.^{31–33} Singlet oxygen and superoxide, as the initial ROS, could also play roles in the oxidation of hydrogenated fullerene through electrophilic substitution and/or addition. However, the exact oxidation mechanism(s) remains unclear

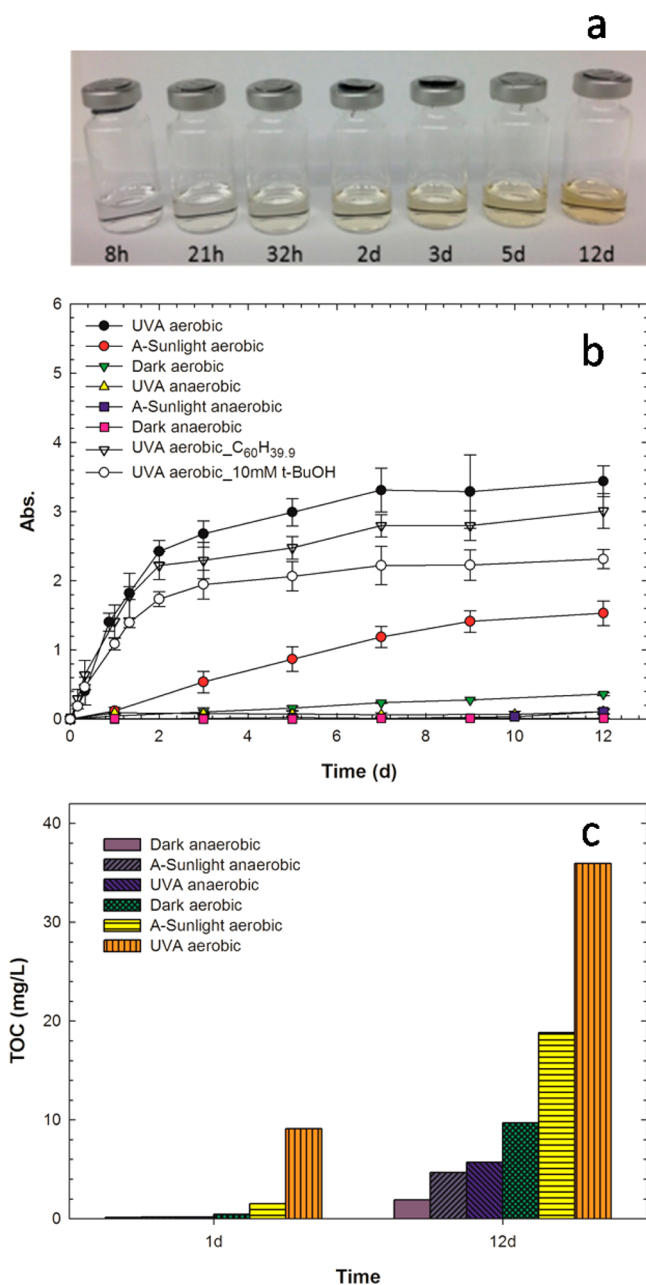


Figure 1. Fullerane solvation experiments. (a) Fullerane product solutions filtered with a $0.45 \mu\text{m}$ membrane over the reaction (UV-A irradiation under ambient conditions). (b) UV maximum adsorption of products as a function of time. (c) Total organic carbon of product solutions after reaction for 1 and 12 days.

and is currently being investigated further. TOC analysis of 1 day and 12 day samples in Figure 1c was consistent with the UV-vis analysis, correlating dissolved carbon with solvation observations. The total organic carbon of soluble products under open, UV-A irradiation reached 36 mg/L after reaction for 12 days, which is 95.7% of the initial solid fullerene carbon added to the reactor. Under the same conditions, the pH correspondingly decreased as the reaction proceeded to a final value of $\text{pH} \sim 4$ due to hydrogen elimination and oxygen-based functional group additions.

Parent fullerene and solvated water-soluble products were characterized by FTIR and compared in Figure 2. Parent fullerene exhibited strong absorption at ~ 2860 and ~ 2780

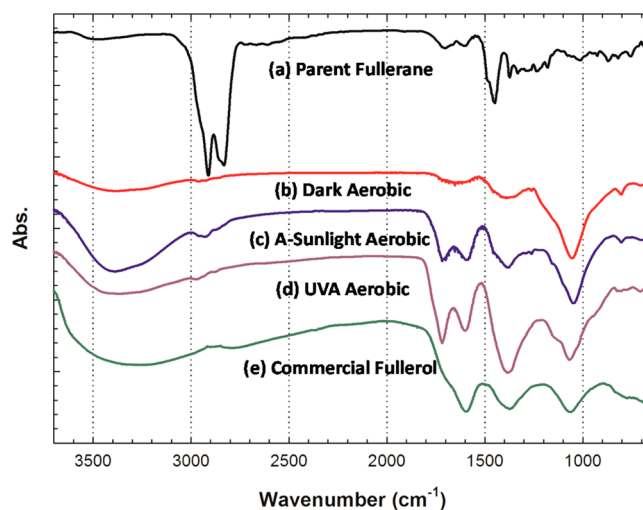


Figure 2. FTIR spectra of unreacted fullerene and products: (a) parent fullerene, (b) products under the dark aerobic condition, (c) products under the attenuated sunlight aerobic condition, (d) products under the UV-A (351 nm) aerobic condition, and (e) commercial fullerol [$\text{C}_{60}(\text{OH})_x(\text{ONa})_y$, where $x + y \sim 24$ (MER Corp.)].

cm^{-1} , values that are assigned to C–H stretching bonds, as reported by Cataldo et al. for $\text{C}_{60}\text{H}_{36}$.²⁷ For all aerobic reaction conditions, a concurrent loss of C–H bonds and the appearance of oxygen functionalities were observed at $\sim 3400 \text{ cm}^{-1}$ (OH stretching) and 1700 cm^{-1} coupled with shifts at 1600 cm^{-1} (C=O), 1400 cm^{-1} (C–OH in-plane bending), and 1050 cm^{-1} (C–O stretching).^{17,29,34,35} The intensities of absorbance peaks typical of carbonyl groups (1700 and 1600 cm^{-1}) and C–OH (1400 cm^{-1}) increased significantly as the light intensity increased (monochromatic UV-A reactions). An IR spectrum of one type of commercial fullerol [$\text{C}_{60}(\text{OH})_x(\text{ONa})_y$, where $y \sim 6-8$, $x + y \sim 24$ (MER Corp.)] is also provided (as the bottom line) in Figure 2 for comparison with that of a well-characterized, water-soluble oxidized fullerene (fullerol), as reported elsewhere.^{17,29,34,36} TEM observations show amorphous, aggregated products cluster, similar to soft aggregated fullerols, as shown by others.³⁷

Product XPS spectra under different reaction conditions are compared in Figure 3. The dominant carbon peak (98.8% peak area) for parent fullerene at a binding energy of 284.5 eV (Figure 3a) is assigned to C–C/C–H carbon,^{38–40} which was also observed in parent C_{60} at a lower ratio (Figure S5 of the Supporting Information). Low levels (1.2%) of (initially) oxidized carbon also appeared in the parent fullerene materials, which has also been observed by others.⁴¹ The XPS spectrum of the products collected from the aerobic reaction in the dark (Figure 3b) showed decreased C–C/C–H signal intensity at 284.5 eV (69.2% peak area) coupled with an increased mono-oxidized carbon signal intensity (286.4 eV , 29.7%).^{39,40} It should be noted that 12 day soluble products, measured as TOC, for aerobic dark conditions were only $\sim 25\%$ (10 mg/L TOC, solubilized) of the original 40 mg/L carbon added as a solid fullerene reactant (Figure 1c). Carbonyl (288.0 eV , 6.2%) and carboxyl groups (289.9 eV , 1.3%) were observed in oxidized products with attenuated sunlight irradiation (Figure 3c).^{17,29,40} Upon UV-A irradiation (Figure 3d), the C–C/C–H ratio of the oxidized products decreased to 68.5% , indicating one-third of the carbon atoms had been oxidized. Additionally,

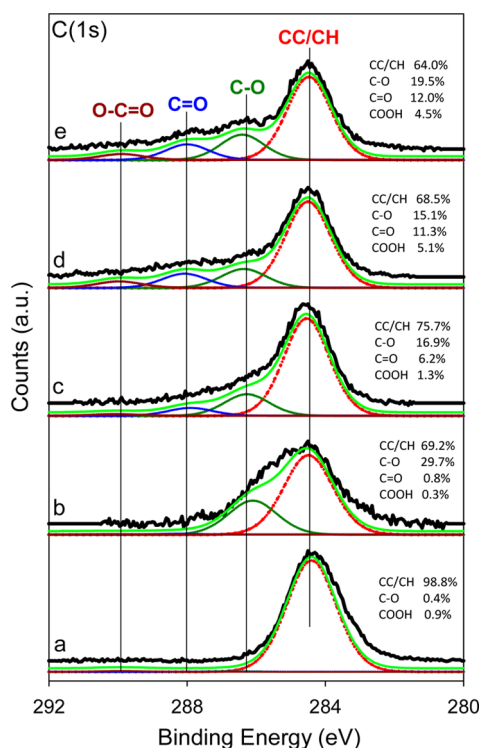


Figure 3. C 1s XPS spectra and curve-fitting analysis of the solvated fullerene products: (a) unreacted fullerene and products from (b) the dark aerobic condition, (c) the attenuated sunlight aerobic condition, and (d) the UV-A aerobic condition, and (e) the commercial fullerol [$C_{60}(OH)_x(OHNa)_y$, where $x + y \sim 24$ (MER Corp.)].

compared to all other conditions, higher levels of carbonyl (C=O, 11.3%) and carboxyl ($-O=C-O$, 5.1%) were observed for these products. XPS analysis of previously described commercial fullerol showed a very similar oxidized carbon distribution compared to that of the UV-A/aerobic (oxidized) fullerene products (Figure 3e).

Upon reaction, the hydrodynamic size of water stable product clusters was evaluated by DLS (Figure S6a of the Supporting Information). The cluster size (number-average) decreased over the reaction time for all aerobic conditions. Smaller size distributions suggest looser aggregation or disaggregation of clustered products as the solvation proceeds, because of a molecular enhancement of water solubility (i.e., increasing oxygen functionality as noted by others).^{42,43} After reaction for 5 days, the average cluster size of the products under UV-A/aerobic irradiation was reduced to 39 nm compared to that under dark aerobic conditions, which was measured to be 95 nm. Stable clusters formed under attenuated sunlight irradiation and exhibited broader size distributions, compared with that under UV-A/aerobic and dark/aerobic conditions. Such polydispersity may be due to the diversity (and varied reaction kinetics) of the soluble products generated upon exposure to a broader spectrum of wavelengths associated with sunlight irradiation. In a study by Hou et al. on the aqueous C_{60} cluster phototransformation, it was demonstrated that the quantum yields and ROS production depend on the wavelength of the irradiating lights,³⁸ which could further affect the oxygen moiety distribution in the products, thus also affecting the relative driving force for cluster formation in the aqueous phase.³⁷ Product partitioning behavior was evaluated via octanol–water partition (expressed as K_{ow}) experiments

(Figure S6b of the Supporting Information). As expected, a significantly decreased K_{ow} was observed for reacted products, which is consistent with the presence of oxygen-based functional groups and thus enhanced aqueous solubility. Partition coefficients for products formed under UV-A/aerobic conditions approach a K_{ow} of zero.

In summary, this study, for the first time, demonstrates that insoluble solid hydrogenated fullerene readily undergoes extensive oxidation and corresponding solvation (solubility) into water in the presence of oxygen. For all reactions, enhancement was observed in the presence of light. Product characterization indicates a significant loss of hydrogen groups along with extensive addition(s) of oxygen-based functionalities. Further, the extent of oxidation was correlated with photoirradiation conditions; a higher light intensity resulted in nearly complete reactant solvation (after 12 days) with higher product oxidation levels and the lowest K_{ow} values. In addition to the role of hydroxyl radical, experiments aimed at a specific (molecular) mechanistic understanding of these reactions are currently ongoing and will be detailed in future reports. On the basis of these key initial observations, significant fullerene reactivity and transformation under aqueous conditions, which include oxygen and light, should be expected to occur. For these and other advanced materials, understanding such reactivity is critical for material fate, transport, and exposure models used for accurate life cycle and risk analyses.

■ ASSOCIATED CONTENT

📄 Supporting Information

Six supporting figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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