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Invited paper

Hydroxyl radical generation with a high power ultraviolet light emitting diode (UV-LED) and application for determination of hydroxyl radical reaction rate constants

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ABSTRACT

We propose a simple, efficient and selective hydroxyl radical generation system based on the photolysis of submicromolar concentrations of nitrite using a high-power ultraviolet light emitting diode (UV-LED). Hydroxyl radical formation by the 6.75-W UV-LED was at least 10 times greater than that by a 300-W Xe lamp. In the UV-LED system, the hydroxyl radical formation rate from nitrite was about four orders of magnitude larger than that from nitrate and two orders of magnitude larger than that from hydrogen peroxide. Such efficient and selective hydroxyl radical formation can be attributed to the overlap of the emission spectrum of the UV-LED and absorption of nitrite. The system was used to determine the reaction rate constants between hydroxyl radicals and chemicals based on the competition method with terephthalate as the hydroxyl radical probe. The reaction rate constants between hydroxyl radicals and some low-molecular-weight organic compounds and inorganic halide salts with various reaction rate constants were determined. The values obtained ranged from 10^5 to $10^{10}\,M^{-1}\,s^{-1}$, and agreed well with previously reported values. The potential of the developed method to determine the reaction rate constants of hydroxyl radicals is discussed.

1. Introduction

Short-lived reactive oxygen and nitrogen species such as hydroxyl radicals [1–3], superoxide anions [4], hydrogen peroxide [5,6] and nitric oxide [7–9] are photochemically generated in water in the natural environment. The hydroxyl radical, which is the most oxidative free radical, is generated by photolysis of nitrate, nitrite and hydrogen peroxide under natural sunlight [1–3] as well as by the photochemical reaction of dissolved organic compounds in natural water [2,3]. The photo-Fenton and Fenton-like processes involving a transition metal such as iron or copper also generate hydroxyl radicals [10]. Because of its strong oxidizing potential, the hydroxyl radical reacts with many molecules with a high reaction rate constant. Therefore, the hydroxyl radical plays major roles in the transformation and degradation of organic compounds. Particularly for persistent organic pollutants, which resist chemical, biological and photochemical degradation in natural environments, degradation by hydroxyl radicals can act as an important possible sink in natural environments. Nakatani et al. studied the photochemical degradation of bisphenol A in river water, finding that hydroxyl radicals strongly influence the lifetime of bisphenol A in the natural environment [11]. It is widely accepted that the presence of hydroxyl radicals can strongly influence the fates of natural and anthropogenic compounds discharged in water environments [12–14]. The reaction rate constant between a hydroxyl radical and chemical species in an aqueous environment is a crucial parameter to characterize and understand the behavior of pollutants. Because the hydroxyl radical is a toxic reactive oxygen species in biological systems, it is a potent agent that can cause many pathological effects and aging. The reactions of hydroxyl radicals with biomolecules can lead to lethal damage in biological systems. The scavenging of hydroxyl radicals in vivo and

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in vitro is of considerable interest in life sciences and medicine. Evaluation of the reaction rate constants of hydroxyl radicals and chemical species in biological media is thus an important task.

Numerous attempts have been made to determine the reaction rate constants between hydroxyl radicals and chemicals as the antioxidant activities of biomolecules [15–18]. The transient method using gamma ray pulse radiolysis has provided a huge number of data sets to examine the reactions of hydroxyl radicals. Some of them can be conveniently referred to on the website of the Notre Dame Radiation Laboratory (NDRL) of the University of Notre Dame, USA, in collaboration with the National Institute of Standards and Technology (NIST), USA [19].

Steady-state methods based on competitive kinetics are commonly used to determine reaction rate constants. In such steady-state methods, hydroxyl radicals competitively react with a probe compound (or reference substance) and target compound, resulting in the formation of a stable product from the reaction between the hydroxyl radicals and probe compound. Many probe compounds to detect hydroxyl radicals have been reported, including highly sensitive fluorescent probes, such as terephthalate (TP) [15,17,20–22], coumarin [16], 3-hydroxycoumarin [23], benzoate [24,25] and benzene [3,11]. These probes react with hydroxyl radicals with high reaction rate constants ($>10^9\,M^{-1}\,s^{-1}$), and generate stable fluorescent products. A hydroxyl radical generation system is also an essential element for the competitive method. The Fenton reaction, photolysis, and radiolysis have been used to generate hydroxyl radicals. Louit et al. developed a fluorometric assay to determine hydroxyl radical reaction rate constants using a ^{137}Cs gamma-ray source with coumarin [16]. They used a multi-well microplate for radiolysis to realize a simple, rapid, high-throughput screening method of antioxidants, although a gamma-ray source with N_2O gas was essential. The Fenton system using hydrogen peroxide and Fe(II) or Fe(II)–ethylenediaminetetraacetic acid (EDTA) chelate has been frequently used to evaluate hydroxyl radical scavenging capacity [15,17,18]. However, the reaction mixtures contain submillimolar-order ferrous compound and hydrogen peroxide, which can scavenge the hydroxyl radicals and cause unexpected reactions. The simple method to assess the relative reactivities of hydroxyl radicals scavenging were also developed, and were applied to the biological and medical fields [26,27].

The 2014 Nobel Prize for physics was awarded to three Japanese scientists, Isamu Akasaki, Hiroshi Amano and Shuji Nakamura, who invented an efficient blue light emitting diode (LED). Their achievements have been used to develop short-wavelength LEDs that emit in the ultraviolet (UV) region. Recently, high-power, low-cost, long-lived UV-LED elements have become available on the market. In this study, we propose a simple photolysis system to generate hydroxyl radicals using a UV-LED. This system is used to determine the reaction rate constant between hydroxyl radicals and chemicals. The high-power 365-nm UV-LED used here generates hydroxyl radicals by photolysis of submicromolar nitrite aqueous solutions with an absorption maximum located at around 355 nm [28,29].

$$NO_2^- + H_2O + h\nu \rightarrow {}^{\bullet}OH + NO + OH^-$$

We use TP as the hydroxyl radical probe, which is readily soluble in water at neutral pH, stable, and not fluorescent and has low toxicity. TP reacts with hydroxyl radicals with a reaction rate constant of $3.3\text{–}4.4 \times 10^9\,M^{-1}\,s^{-1}$ to quantitatively form a strongly fluorescent product, 2-hydroxyterephthalate (HTP) [20–22]. We examine the features of hydroxyl radical generation by the UV-LED, and the potential of the method to determine the reaction rate constants of hydroxyl radicals.

2. Material and methods

2.1. Reagents

TP and HTP were obtained from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). Other chemicals and solvents were of reagent or HPLC grade, and used without further purification. All solutions were made using ultrapure water obtained from a Milli-Q Elix UV-5 and Milli-Q Advantage (Millipore, Tokyo, Japan).

2.2. UV-LED light source

The UV-LED was purchased from Nitride Semiconductors Co. Ltd (NS365L-6SMG, Naruto, Japan). According to the specification sheet of the UV-LED, its typical peak wavelength is 360–370 nm, full width at half-maximum is 9 nm, and typical optical output power is 2750 mW at a DC forward current of 1.0 A. The UV-LED was installed on an aluminum heat sink with a cooling fan driven by a custom-made constant-current power supply at a DC forward current of 0.9 A and forward voltage of 7.4–7.6 V.

2.3. Batch photochemical experiments

Photochemical experiments with a quartz photochemical reaction cell were conducted by the batch method to characterize hydroxyl radical formation using the UV-LED and compared with that by a solar simulator equipped with a Xe lamp. The quartz photochemical reaction cell, which was custom-made at our university, was 80 mm in diameter and 12 mm thick (optical path). The UV-LED was placed 10–15 mm above the top surface of the reaction cell. All of the experiments were conducted in air-saturated condition at room temperature.

A solar simulator (81160-1000, Oriel, USA) equipped with a 300-W ozone-free Xe lamp was also used as the light source. The light intensity of the solar simulator was estimated using chemical actinometry based on the photochemical degradation of 2-nitrobenzaldehyde (2-NB). The degradation rate of 2-NB by the solar simulator was estimated to be $0.0042\,s^{-1}$. The degradation rate of 2-NB by sunlight on October 7, 2002 at Higashi-Hiroshima (at noon under clear sky conditions) was $0.0093\,s^{-1}$, suggesting that the light intensity of the solar simulator was about 45% of natural sunlight at noon under a clear sky.

2.4. Determination of the rate constants of the reaction between hydroxyl radicals and target compounds based on the competition method

In a sample mixture including the target compound (X) and TP as a probe compound (Supplementary content), the fraction of hydroxyl radicals that reacted with TP in the competition with the target compound was,

$$f_{OH} = \frac{k_{TP,OH}[\mathrm{TP}]}{k_{TP,OH}[\mathrm{TP}] + k_{X,OH}[\mathrm{X}] + \sum k_{Scav-i,OH}[\mathrm{Scav-i}]}, \qquad (1)$$

where $k_{TP,OH}$ and [TP] are the reaction rate constant and concentration of TP, respectively, and $k_{X,OH}$ and [X] are the reaction rate constant and concentration of the target compound, respectively. $k_{Scav\text{-}i,OH}$ and [Scav-i] are the reaction rate constant and concentration of hydroxyl radical scavengers other than TP and the target compound, respectively. The third term of the denominator, $\sum k_{Scav\text{-}i}$ [Scav-i], is the subtotal of the scavenging rate by all of the scavengers in the reaction mixture except TP and the target compound, which include the hydroxyl radical source (nitrite), components of the buffer solution (when used) and other unknown scavengers in the reaction mixture. After generation of