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Fluorescent Signaling of Oxone by Desulfurization of Thioamide

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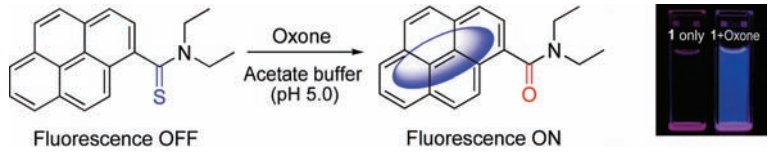
ABSTRACT



The chemosignaling of the oxidant Oxone by selective desulfurization of a thioamide was investigated. Pyrene-thioamide was efficiently converted to its amide analogue by reaction with Oxone, resulting in a pronounced fluorescent turn-on type signaling. Selective signaling of Oxone in aqueous solution was possible in the presence of representative alkali and alkaline earth metal ions, as well as common anions.

The search for selective and efficient signaling systems to detect various chemically and biologically pertinent species is an important area of research.[1] In particular, the signaling of a variety of biologically significant oxidants, such as hydrogen peroxide,[2] hypochlorous acid,[3] and peroxynitrite,[4] has attracted much research interest. However, convenient signaling of more practical oxidants, including peracids and peroxymonosulfates, has been less thoroughly studied.[5]

Among many sophisticated signaling systems, chemodosimeters have received much interest due to their specificity and cumulative signaling effects.[6] There are many smart probe systems for the analysis of metal ions which utilize metal ion-induced desulfurization and/or ring forming reactions.[7] In particular, desulfurization of thioamides to the amide analogues has been utilized as the signaling basis for Hg^{2+} and Ag^{+}.[8,9]

Potassium peroxymonosulfate is a component of a triple salt with the formula $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$ that is known by the trade name Oxone. Oxone is widely used as an oxidizing agent for a variety of consumer applications:[10] an animal sanitizer, denture cleanser, and nonchlorine oxidizer for swimming pools and spas.[11] In addition, it is used for industrial applications,[12] such as circuit board etchants, pulp recycling, wood cleaning, and oxidation of reduced sulfur and cyanide in wastewater treatment. In synthetic organic

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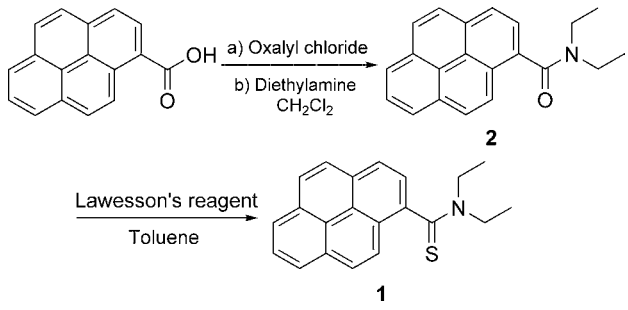
chemistry, Oxone is a versatile oxidant for the conversion of aldehydes to carboxylic acids[13] and for the epoxidation of alkenes.[14] Oxone also oxidizes thioethers to sulfones,[15] pyridine to pyridine-*N*-oxide,[16] and amines to nitroxides.[17] Especially, Oxone has been used as a convenient and inexpensive oxidant for the conversion of thiocarbonyl compounds, including thioamides, thioureas, and thioesters, to the corresponding oxo derivatives.[18]

Measuring an exact concentration of Oxone is required for precise monitoring of this oxidant in swimming pools, consumer products, and other industrial processes. Currently, it can be analyzed by a standard iodometric titration or by treatment with excess ferrous ammonium sulfate, followed by back-titration with standardized potassium permanganate or ceric sulfate solution.[19] Although Oxone is widely applied, a convenient optical method for its detection has not yet been reported. In this regard, a simple and inexpensive Oxone sensitive optical detection method is desirable. We devised a simple fluorescent signaling system for Oxone using the desulfurization of a thioamide derivative of pyrene. The designed pyrene thioamide derivative exhibited an efficient and selective fluorescent signaling of Oxone in an aqueous environment.

Pyrene-diethylamide **2** was prepared by the reaction of 1-pyrenecarboxylic acid with diethylamine (oxalyl chloride, CH_2Cl_2) (Scheme 1). Thioamide derivative **1** was obtained

Scheme 1. Preparation of Pyrene-Thioamide **1**



by the treatment of **2** with Lawesson's reagent in good yield (78%). An interesting observation in the ^{1}H NMR spectra of thioamide **1** and amide **2** was the diastereotopic behavior of the methylene protons of the ethyl group. One of the methylene protons of **1** gave a pair of multiplets at 4.09 and 4.61 ppm (Figure S1, Supporting Information). This phenomenon might be due to restricted rotation about the C−C bond of the pyrene−C−C═S moiety, because of the bulky pyrene moiety.[20] As a result of this restricted rotation, the methylene protons situated near the pyrene group become diastereotopic and yield a pair of multiplets in the NMR spectrum. For a similar reason, compound **2** also showed a pair of multiplets at 3.65 and 3.92 ppm for one of the methylene protons of the ethyl group (Figure S2, Supporting Information).

Interaction of thioamide **1** with Oxone revealed considerable changes in its UV−vis spectral behavior (Figure S3, Supporting Information). Upon treatment of **1** with Oxone in aqueous acetonitrile solution (acetate buffered H_2O: CH_3CN = 9:1, v/v), the absorption bands of **1** at 334 and 349 nm were slightly blue-shifted to 325 and 341 nm.

Compound **1** exhibited very weak fluorescence emission around 385 nm in 90% aqueous acetonitrile solution buffered at pH 5.0 with an acetate buffer (Figure 1). The weak emission

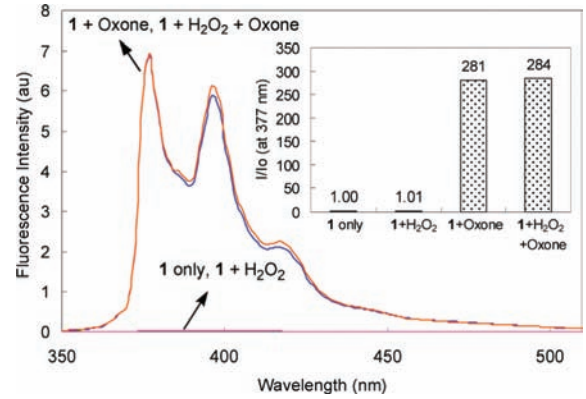


Figure 1. Fluorescence spectra of **1**, **1** in the presence of Oxone, H_2O_2, or H_2O_2 and Oxone. [**1**] = 5.0×10^{-6} M. [Oxone] = [H_2O_2] = 5.0×10^{-4} M in a mixture of CH_3CN and acetate buffer solution (pH 5.0, 10 mM) (10:90, v/v). λ_{ex} = 340 nm.

of **1** is due to the presence of the thiocarbonyl sulfur atom.[21] Though compound **1** showed rather similar fluorescence enhancement between pH 3 and 10 (Figure S4, Supporting Information), acetate buffer was used because amine containing hepes or tris buffer might react with Oxone.[22] Upon interaction with Oxone, a large fluorescence enhancement was observed, and the colorless solution revealed a bright blue color under illumination with a UV lamp. The ratio I/I_o, where I and I_o represent the fluorescence intensity in the presence and absence of analytes, measured at 377 nm, was 281 for Oxone. On the other hand, another important oxidant, hydrogen peroxide, had only a negligible effect on the fluorescence of **1**, and its I/I_o was 1.01. Meanwhile, compound **1** revealed rather nonselective

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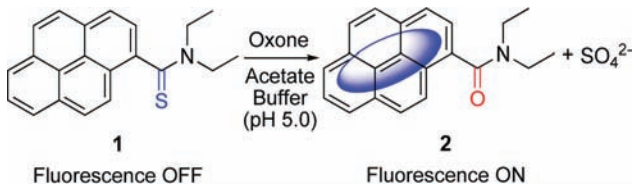
responses toward other important oxidants of hypochlorite, peracetic acid, and superoxide (Figure S5, Supporting Information). However, Oxone is generally used as a single oxidant in many applications, where selectivity over other oxidants is not so crucial for the selective determination of Oxone.

Signaling is thought to occur by the selective desulfurization of thioamide **1** to the amide by reaction with Oxone (Scheme 2). The sulfur atom of **1** is converted to sulfate as

Scheme 2. Signaling of Oxone by Pyrene-Thioamide **1**



an oxidized byproduct.[18a] The quenching effect of the thiocarbonyl sulfur atom resulted in a very weak fluorescence of the pyrene fluorophore. Upon transformation to the oxo amide, this sulfur-quenching effect was removed with the concomitant restoration of pyrene fluorescence. Evidence for the proposed chemical transformation was provided by ^{13}C NMR, UV−vis, and fluorescence measurements. The ^{13}C NMR spectrum of the product obtained by the treatment of **1** with 2 equiv of Oxone was almost identical with that of **2** (Figure 2). In addition to this, the UV−vis and fluorescence

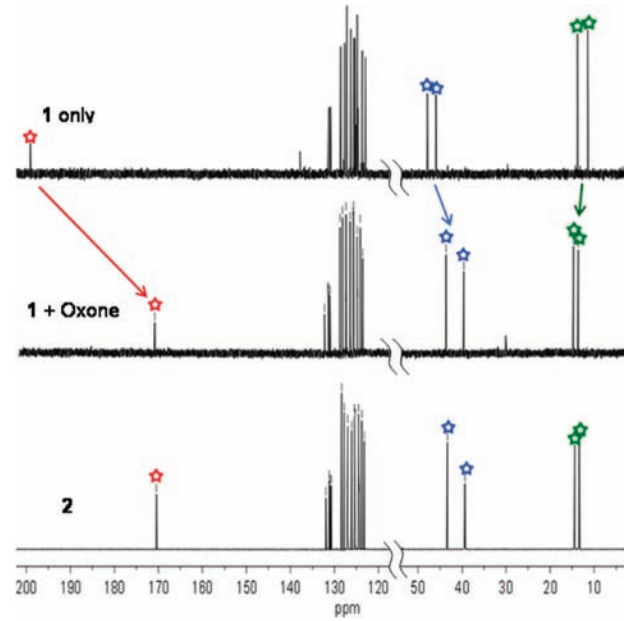


Figure 2. Partial ^{13}C NMR spectra of **1**, **1** upon the reaction with Oxone, and **2** in $CDCl_3$. [**1**] = [**2**] = 3.0×10^{-2} M. Middle spectrum (**1** + Oxone) was obtained from a purified product of the reaction of **1** with Oxone (2 equiv) in aqueous acetonitrile solution.

spectra of **1** in the presence of Oxone were almost the same as those of **2** (Figures S3 and S6, Supporting Information).[23]

Signaling of Oxone by **1** was fairly fast, requiring less than 10 min to obtain a constant signal (Figure S7, Supporting Information). On the other hand, in the absence of Oxone, compound **1** was stable, and its fluorescence behavior did not change appreciably even 24 h after sample preparation. Fluorescence titration of **1** with varying amounts of Oxone afforded a linear calibration curve up to 2 equiv of Oxone (Figure 3). From this titration curve, the detection limit for

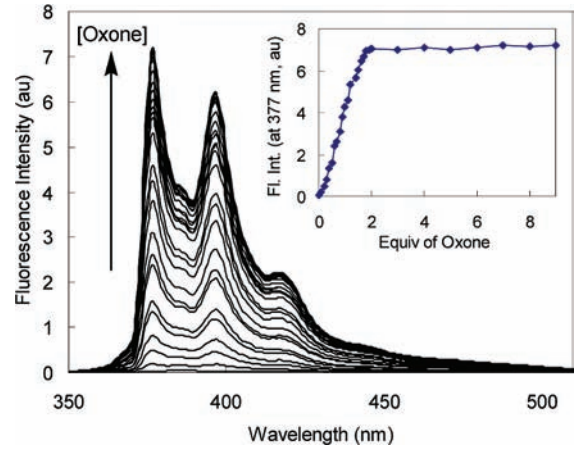


Figure 3. Fluorescence titration of **1** with Oxone. [**1**] = 5.0×10^{-6} M in a mixture of CH_3CN and acetate buffer solution (pH 5.0, 10 mM) (10:90, v/v). λ_{ex} = 340 nm.

the analysis of Oxone was estimated to be 1.9×10^{-6} M (1.2 ppm) in 90% aqueous acetonitrile solution.[24] This detection limit for thioamide **1** is well below the Oxone concentration used as a nonchlorine oxidizer in swimming pools (~20 ppm).[19]

Finally, potential interferences from coexisting metal ions and anions generally found in natural or tap water on Oxone signaling by **1** were surveyed (Figure 4). Interference by coexisting ions might originate from accelerated decomposition of Oxone or side reactions with Oxone to form undesirable products. No interference with the signaling of Oxone by **1** was noticed from frequently encountered alkali and alkaline earth metal ions (Na^+, K^+, Mg^{2+}, and Ca^{2+}) as well as common anions, including chloride, nitrate, and sulfate. Potentially catalytic transition metal ions, such as manganese, cobalt, and nickel, were ruled out of the survey, since they are known to accelerate the decomposition of Oxone.[25] Bromide and iodide ions were not tested either because Oxone can oxidize these halides to the active

(23) Compound **1**: λ_{max} = 349 nm, $\epsilon = 1.7 \times 10^4$ $M^{-1}cm^{-1}$. Φ = 0.0001. Compound **2**: λ_{max} = 341 nm, $\varepsilon = 3.2 \times 10^4$ M^{-1} cm^{-1}. Φ = 0.11 in 90% aqueous acetonitrile at pH 5.0. Reported quantum yields are based on anthracene, Φ = 0.27 in ethanol: Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229.

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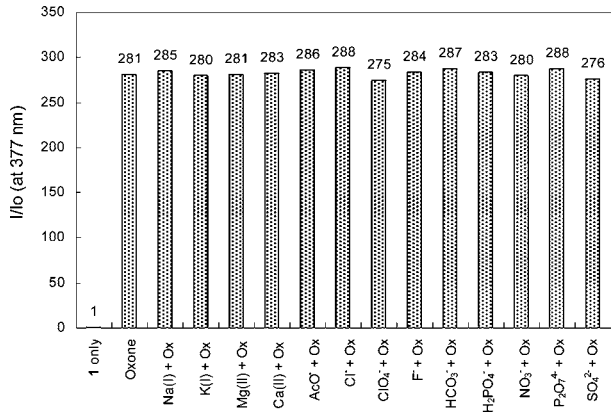

Figure 4. Fluorescent signaling of Oxone by **1** in the presence of representative metal ions and anions. Measured at 377 nm. [**1**] = 5.0×10^{-6} M. [Oxone] = 5.0×10^{-5} M. $[M^{n+}] = [A^{n-}] = 5.0 \times 10^{-4}$ M. In a mixture of CH_3CN and acetate buffer solution (pH 5.0, 10 mM) (10:90, v/v). $\lambda_{ex} = 340$ nm. Ox = Oxone.

halogens (bromide to bromine[26] and iodide to iodine[27]). Even though thioamide is well-known to react with mercury and silver ions,[8,9,28] compound **1** did not show any significant fluorescence changes with those cations as well as other metal ions (Figure S8, Supporting Information). The time trace plot also confirmed the low reactivity of compound **1** with silver or mercury ions, which might be due to the steric congestion around the thiocarbonyl function. Even after 24 h of sample preparation, negligible changes in the absorption and fluorescence spectra were observed.

In summary, a new simple chemosignaling system for the widely used oxidant Oxone was devised based on a thioamide to amide transformation. A pyrene-thioamide derivative showed pronounced signaling of Oxone in the micromolar concentration range in aqueous solution. The designed compound also exhibited efficient Oxone-selective fluorescent signaling behavior in the presence of common metal ions and anions, as well as hydrogen peroxide.

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Supporting Information Available: Experimental details, NMR spectra, chemosignaling behavior, and UV−vis and fluorescence data. This material is available free of charge via the Internet at http://pubs.acs.org.

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