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Journal of Photochemistry and Photobiology A: Chemistry 181 (2006) 238–245
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Chemiluminescence of cerium(IV)–rhodamine 6G–phenolic compound system

Hua Cui *, Qunlin Zhang, Aung Myint, Xuewu Ge, Lijuan Liu

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, PR China

Received 27 June 2005; received in revised form 29 September 2005; accepted 1 December 2005
Available online 4 January 2006

Abstract

The oxidation reaction between cerium(IV) and rhodamine 6G in sulfuric acid medium underwent weak chemiluminescence (CL). The effects of 53 organic compounds of interest on cerium(IV)–rhodamine 6G chemiluminescence were investigated by a flow injection procedure, and 32 phenolic compounds were found to enhance CL. Phenolic compounds mainly include phenols, polyphenols, phenolic acids, hydroxycinnamic acids and flavonoids. The correlation between CL and molecular structure was systematically studied. It was noteworthy that phenolic hydroxyls were the main active groups for the generation of CL. The magnitude of CL was related to the type and position of substituents in the benzene ring. The maximal emission wavelength of CL spectra for all tested phenolic compounds was at about 555 nm, and luminophors were assigned to rhodamine 6G. Based on the studies of kinetic process and the spectra of CL, fluorescence and UV–vis absorption, a CL mechanism has been proposed to be due to that rhodamine 6G and phenolic compound are oxidized by cerium(IV) to form the excited-state cerium(III), which transfers energy to rhodamine 6G, resulting in light emission. However, on the other hand, if the oxidation products of some phenolic compounds such as benzoquinone or ketone could significantly quench the emissive rhodamine 6G via energy transfer, no light emission was observed for such compounds as hydroquinone and catechol.

Keywords: Chemiluminescence; Cerium(IV); Rhodamine 6G; Phenolic compound

1. Introduction

There are some reports in the literature regarding the use of cerium(IV)–rhodamine chemiluminescence (CL) system for the determination of glutathione [1], captoril [2,3], chlorpromazine hydrochloride [4], flurosemide [5], phenothiazines [6], folic acid [7], analgin [8], tiopronin [9], hydrochlorothiazide [10], ceph-based β-lactam antibiotics [11], phentolamine [12], ascorbic acid [13] and DNA [14,15]. Most of these analytes are N- or S-containing compounds, but phenolic compounds (PCs) have not been systematically studied. In the most cases, including glutathione [1], captoril [2,3], chlorpromazine hydrochloride [4], flurosemide [5], phenothiazines [6], folic acid [7], analgin [8], tiopronin [9], hydrochlorothiazide [10], ceph-based β-lactam antibiotics [11] and phentolamine [12], rhodamine was used as a sensitizer, and the possible mechanism can be expressed as Scheme 1. In Scheme 1 SP represents glutathione, captoril, chlorpromazine hydrochloride, flurosemide, phenothiazines, folic acid, analgin, tiopronin, hydrochlorothiazide, ceph-based β-lactam antibiotics and phentolamine; SP_{OX}, the oxidized form of SP; Rho, rhodamine 6G or B.

For ascorbic acid [13], the oxidation product of rhodamine B was served as luminophor. The pathways can be described as Scheme 2. In Scheme 2 Rho B is rhodamine B; H_2A, the ascorbic acid; $[^{\bullet}\text{Rho B}^{-}]^{*}_{ox}$, the rhodamine B luminophor with negative oxygen ion.

For DNA [14], the oxidation product of the complex between rhodamine B and DNA was luminophor. The reaction scheme is (Scheme 3).

PCs occur as secondary metabolites in all plants [16] and embrace a considerable range of substances possessing

Abbreviations: CL, chemiluminescence; FI, flow injection; PC(s), phenolic compound(s)

* Corresponding author. Tel.: +86 551 3606645; fax: +86 551 3601592.
E-mail address: hcui@ustc.edu.cn (H. Cui).

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doi:10.1016/j.jphotochem.2005.12.003

$$Ce(IV) + SP \longrightarrow Ce(III)^{*} + SP_{ox}$$
$$Ce(III)^{*} + Rho \longrightarrow Ce(III) + Rho^{*}$$
$$Rho^{*} \longrightarrow Rho + h\nu \quad (\lambda = 555\ nm)$$

Scheme 1. The mechanism of the cerium(IV)–rhodamine–SP CL reaction.

$$Rho\ B \xrightarrow[H_2SO_4]{Ce(IV)} [{}^{\bullet}Rho\ B^{-}]^{*}_{OX} \longrightarrow [{}^{\bullet}Rho\ B^{-}]_{OX} + h\nu \quad (\lambda = 420\ nm)$$
$$H_2A \xrightarrow[H_2SO_4]{Ce(IV)} HA^{\bullet}$$
$$[{}^{\bullet}Rho\ B^{-}]_{OX} + HA^{\bullet} \xrightarrow[H_2SO_4]{Ce(IV)} [{}^{\bullet}Rho\ B^{-}]^{*}_{OX} + H^{+} + A$$

Scheme 2. The mechanism of the cerium(IV)–rhodamine B–H_2A CL reaction.

an aromatic ring bearing one or more hydroxy substituents. These compounds mainly include phenols, polyphenols, phenolic acids, hydroxycinnamic acids and flavonoids. They have received considered attention as the potentially protective factors against cancer and heart disease in part because of their potent antioxidative properties and their ubiquity in a wide range of commonly consumed foods of plant origin [17,18]. Up to now, knowledge of the levels of these compounds in plants is of considerable interest but is limited by the problems of analysis [19]. Lately, more interest has been shown in PCs due to their possible additional health benefits. Moreover, PCs are environmentally important compounds. Therefore, it is very important to develop highly sensitive analytical methods for the analysis of PCs.

CL techniques have received much attention because high sensitivity and wide linear range can be reached with simple instrumentation. However, only limited analytes can be detected using CL techniques due to fewer CL reactions available. Therefore, it is a great challenge for chemists to develop new CL reactions with wide application and expand the applicable scope of the existent CL reactions. In our previous work, it was found that the oxidation reaction between cerium(IV) and rhodamine 6G in sulfuric acid medium generated weak CL, which could be strongly enhanced by parabens [20]. In this paper, the effects of 53 organic compounds of interest on the cerium(IV)-rhodamine 6G CL were examined by a flow injection (FI) procedure and 32 PCs were found to enhance CL. The correlation between CL and molecular structure was systematically studied. The kinetic process and the spectra of CL, fluorescence, and UV–vis absorption were analyzed, and a CL mechanism was proposed.

$$DNA + Ce(IV) \xrightarrow{H_2SO_4} [Ce(IV)\text{-}DNA]$$
$$[Ce(IV)\text{-}DNA] + Rho\ B \longrightarrow [Rho\ B\text{-}DNA\text{-}Ce(IV)]$$
$$\xrightarrow{electron\text{-}transfer} [DNA\text{-}Rho\ B^{-}]^{*}_{OX} + Ce(III)$$
$$[DNA\text{-}Rho\ B^{-}]^{*}_{OX} \longrightarrow [DNA\text{-}Rho\ B^{-}]_{OX} + h? \quad (\lambda = 300\ nm)$$

Scheme 3. The mechanism of the cerium(IV)–rhodamine B–DNA CL reaction.

2. Experimental

2.1. Reagent

All chemicals were of analytical grade, and redistilled water was used throughout. Cerium(IV) sulphate tetrahydrate was obtained from Shanghai Yaolong Metal Company (Shanghai, China) and prepared in sulfuric acid solution daily. Rhodamine 6G and 4-hydroxy-3,5-dimethoxybenzoic acid were obtained from Merck (Darmstadt, Germany). Chlorogenic acid was purchased from Roth Chem. (Karlsruhe, Germany). 3,5-Dihydroxybenzoic acid, *m*-hydroxybenzoic acid and 4-hydroxy-3-methoxybenzyl alcohol were purchased from Fluka Chemie (Bucks, Switzerland). 2,3-Dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid and 4-hydroxy-3-methoxybenzoic acid were purchased from Acros Organics (Fairlawn, NJ, USA). All tested flavonoids were obtained from Chinese National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). The other chemicals were purchased from Shanghai Reagents (Shanghai, China). The stock solution of 1.0×10^{-3} mol/l rhodamine 6G was prepared with redistilled water. The stock solutions of 1.0×10^{-4} g/ml phenolic compounds were prepared with redistilled water or methanol and standard solutions by diluting with redistilled water. The solutions of phenolic compounds were all stored in the dark at 0–4 °C, which was stable during 1 month.

2.2. Apparatus

CL measurements were made using a flow injection CL analyzer consisting of a model FIA-2400 flow injection system (Xintong, Beijing, China), a model 1P-21 photomultiplier tube (Binsong, Beijing, China) biased at −850 V and a model GD-1 luminometer (Ruike, Xi′an, China). The flow cell was a flat coil placed in front of photomultiplier tube. An IBM compatible personal computer was used for data acquisition. The CL and the fluorescent spectra were measured by using a model RF-5301 fluorimeter (Shimadzu, Kyoto, Japan). The UV–vis spectra were conducted on a model UV-2401PC spectrophotometer (Shimadzu, Kyoto, Japan). pH measurement was carried out on a model pHS-3B meter (REX, Shanghai, China).

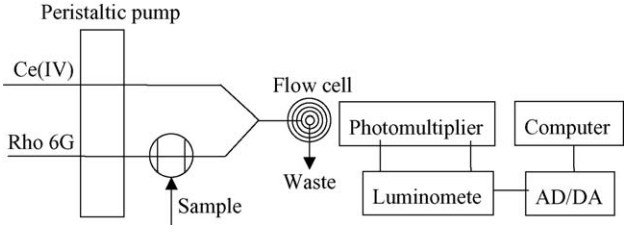

Fig. 1. Schematic diagram of FI–CL system.