



Synthesis and characterization of new oxalate ester–polymer composites for practical applications

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ARTICLE INFO

Article history:

Received 16 June 2012

Received in revised form

1 September 2012

Accepted 21 September 2012

Available online 1 October 2012

Keywords:

Chemiluminescence

Imidazole

Fluorescer

PEG 200

PEG 400

ABSTRACT

The present study focused on the synthesis of high purity oxalate esters: bis(2,4,6-trichlorophenyl) oxalate (TCPO) and bis(2,4,5-trichloro-6-carbobutoxyphenyl) oxalate (TCCBPO), and further on their incorporation into potentially applicative polymer composites. The organic compounds were characterized through NMR and the composites obtained were evaluated for light capacity availability at room temperature and low temperatures. The concentrations of the peroxide, fluorescer, catalyst, and polymer additives were optimized.

The chemiluminescent composites' performances were evaluated after 360 days and returned satisfactory results.

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1. Introduction

The high purity demand for the achievement of chemiluminescent (CL) properties led to the necessity of well-established synthesis and advanced purification strategies. The impurities present in CL systems (CLSs) led to secondary reactions, with negative effects for light-generation reactions—quenching. In this paper, advanced methods for the obtaining of important CL substances are presented. Such studies have tremendous importance [1] since (1) oxalate esters existing in the market are very expensive and, in general, available only on demand, and (2) oxalate esters with carboxyl substituents at the aromatic cycle are not available commercially, due to their low chemical stability and/or strictly specialized applicative potential.

Two oxalate esters were chosen for the present study: bis(2,4,6-trichlorophenyl) oxalate (TCPO) and bis(2,4,5-trichloro-6-carbobutoxyphenyl) oxalate (TCCBPO). The literature indicates the obtainment of oxalate esters starting from oxalyl chloride and different nucleus-substituted phenols or their sodium phenoxides [1–6]. The synthesis strategy considered here that the reagents are accessible; a number of steps lead to a good yield and a highly pure final product.

Therefore, a one-step synthesis was chosen for TCPO, using oxalyl chloride and trichlorophenol as reagents. TCCBPO two-step synthesis used as a main reagent the 2,4,5-trichlorosalicylic acid,

obtaining the *n*-butyl-2,4,5-trichlorosalicylate through esterification of 2,4,5-trichlorosalicylic acid with *n*-butyl alcohol, and obtaining the oxalate ester through the reaction of *n*-butyl-2,4,5-trichlorosalicylate and oxalyl chloride.

Since it was seen that either the literature did not provide detailed procedures for the synthesis of oxalate esters or major differences among those procedures and the experimental results were found, a systematic approach was used for the determination of optimum reaction parameters, in the view of establishing a reproducible laboratory technology for the oxalate esters obtainment, leading to high purity reaction products.

2. Materials and methods

2.1. Materials

For the syntheses, the reagents were used as such, without any further purification: 2,4,6-trichlorophenol 99% from Aldrich, trichlorosalicylic acid 99% from Merck, benzene 99% from Sigma, *n*-butyl alcohol 99% from Fluka, pyridine 99% from Sigma, oxalyl chloride 98% from Aldrich, anhydrous methylic alcohol 98% from Fluka, cyclohexane 98% from Sigma, anhydrous sodium sulfate 99% from Chimopar, anhydrous calcium chloride 98% from Chimopar, sulfuric acid 95% from Merck, and ethylic ether 99% from Fluka.

During the experiments for the achievement of oxalate esters-based CL composites, the following substances were employed: TCPO—synthesized, 99% purity; TCCBPO—synthesized, 99% purity;

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tert-butyl-hydroperoxide 80% from Aldrich; hydrogen peroxide 60% from Aldrich; sodium salicylate (NaSy) 99.5% from Aldrich; dibutylphthalate (DBP) 99% from Aldrich; dimethylphthalate (DMP) 99% from Aldrich; tert-butyl alcohol 99% from Aldrich; polyethyleneglycol PEG 200 and polyethyleneglycol PEG 400 from Aldrich; perylene 99% from Riedel-de-Haen; rubrene 98% from Aldrich; 9,10-diphenylanthracene (DPA) 98% from Aldrich; 9,10-bis(phenylethynyl)-anthracene (BPEA) 97% from Aldrich; and 1-chloro-9,10-bis(phenylethynyl)-anthracene (CIBPEA) 99% from Aldrich.

2.2. Synthesis of TCPO

The TCPO synthesis mainly consisted of the reaction between 2,4,6-trichlorophenol and oxalyl chloride, according to the reaction from Fig. 1.

In brief, in a three-neck brown glass reactor equipped with magnetic stirrer, thermometer, dropping funnel, water bath and ascendant refrigerant with CaCl_2 , 2 M of trichlorophenol in 5.6 M of anhydrous benzene was introduced. The mixture was stirred at 25 °C until the complete dissolution of the trichlorophenol; pyridine was added 1:1 M versus trichlorophenol, in order to capture the HCl resulted. A benzene:oxalyl chloride solution (2.4:1.1 M) was poured in the reaction during 1.5 h, under vigorous stirring and maintaining the reaction temperature at 25 °C. After complete dissolution and reaction (2.5 h), the amine chlorohydrate was filtered, and the filtrate was recovered and washed with distilled water. The organic solution was dried on anhydrous sodium sulfate and the benzene was distilled under vacuum (10 mbar) in order to obtain the oxalate ester. TCPO was recrystallized from cyclohexane in order to obtain a 99% pure yellowish-white crystalline product, with the melting point at 191–193 °C.

2.3. Synthesis of TCCBPO

The TCCBPO synthesis from 3,5,6-trichlorosalicylic acid followed two main steps: (a) esterification of 3,5,6-trichlorosalicylic acid with *n*-butanol (Fig. 2(a)), and (b) acylation of *n*-butyl-3,5,6-trichlorosalicylate with oxalyl chloride (Fig. 2(b)).

In a three-neck brown reactor equipped with magnetic stirrer, thermometer, Dean–Stark distilling trap and ascendant refrigerant with CaCl_2 , 0.15 mol of trichlorosalicylic acid and 3.5 ml sulfuric acid were dissolved in 1.2 mol *n*-butanol. The reaction mixture was refluxed at 120–125 °C for 20 h, while removing the water with the

Dean–Stark device, the reaction mixture being afterwards rinsed with water. The organic phase was separated, 50 ml ethylic ether was poured, and the solution obtained was washed with water and separated again. The organic phase that resulted was dried on sodium sulfate and distilled under vacuum (at 10 mbar), obtaining the *n*-butyl ester of the trichlorosalicylic acid, a brownish crystal with the melting point at 34–35 °C and a 79% yield.

Further, in a similar reactor, 0.1 mol of the resulted *n*-butyl ester of the trichlorosalicylic acid and 200 ml of anhydrous benzene were stirred until complete dissolution, at 25 °C. Next, 0.1 mol (8 ml) of pyridine was added. Following this, over the solution in the reactor a solution of 0.11 mol of oxalyl chloride in 250 ml benzene was added dropwise, for 1.5 h, under vigorous stirring and maintaining the temperature at 25 °C. After addition and the achievement of the reaction (~8 h), the amine chlorohydrate formed was filtered and the filtrate was recovered and washed with distilled water. The benzene was distilled under vacuum (10 mbar) and the oxalate ester was crystallized. The TCCBPO was washed with anhydrous methyl alcohol and was recrystallized from cyclohexane in order to obtain a 96% pure white compound, with 72% yield. After a second purification, crystals of 99% purity and melting point of 121–123 °C were obtained, with a final yield of 48%.

2.4. CL producing mixture

The CL composites, achieved directly in 10 ml glass vials, contained the oxalate ester synthesized, hydrogen peroxide, a fluorescent compound, a catalyst, and a solvent. Experimental tests were performed in order to establish the fluorescers available for those CL composites that emit in the visible spectrum, in order to maximize the scotopic visual sensitivity efficiency. Determinations were performed on the most efficient fluorescers available commercially [5–8]: perylene, rubrene, CIBPEA, and BPEA. Imidazole was used as catalyst, due to its high performance results regarding reproducibility and solubility both in organic solvents and water. In its presence, the reaction rate was determined by the replacement of the first aryl radical of the oxalate ester by the base, followed by the rapid replacement of the second aryl radical and formation of 1,1'-oxalyl diimidazol (ODI) [6,8–12]. DMP and DBP were employed as solvents, in order to ensure an adequate solubility of the fluorescent reagents.

2.5. Products characterization

The organic products obtained were analyzed through NMR, using a Varian Gemini 2000–2300 MHz spectrometer, at room temperature, the chemical shifts being considered in delta values versus the solvent used (CDCl_3 in case of TCPO): ^1H —7.27 ppm (DMSO in case of TCCBPO): ^1H —2.49 ppm. The correct assignment of the chemical shifts was obtained in the latter case through COSY experiments.

Fluorescence determinations were performed on a UNICAM Helios absorption spectrometer, and a JASCO FP-6300 spectrofluorimeter within the range 220–750 nm.

2.6. Evaluation of CL composites versus scotopic visual sensitivity

The counter was started right after putting the reagents together. The mixtures were vortexed using a Wizard VELD Scientifica for 5 min, at 1200 rpm. Afterwards, the vial was introduced in the measurement device, at 150 mm in front of an Extech HD 450 detector sensor (Extech Instruments Corporation, Nashua, USA). The data were stored automatically in the internal memory of the device. When the experiment was finished, the recording stopped and the data were saved for further processing with Microcal™ Origin® software (Microcal Software Inc., Northampton, USA), in the view of

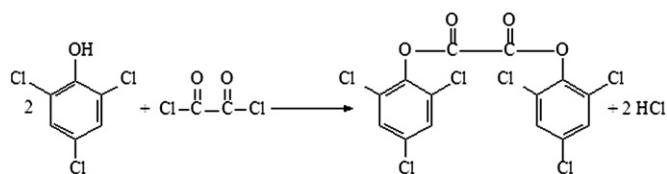


Fig. 1. TCPO synthesis.

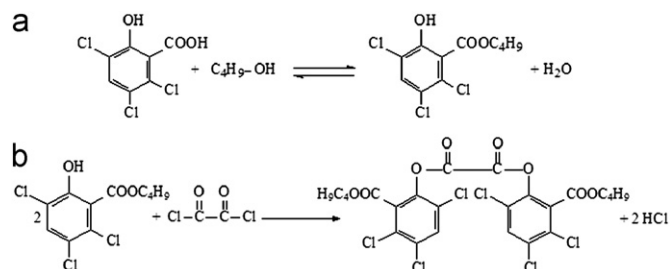


Fig. 2. TCCBPO synthesis: (a) esterification; and (b) acylation.

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