



## Photooxidation of camphorquinone in polystyrene matrix

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### ARTICLE INFO

#### Article history:

Received 18 May 2011

Received in revised form 17 August 2011

Accepted 20 August 2011

Available online 3 September 2011

#### Keywords:

Camphorquinone

1,2-Diketone

Polystyrene

Photooxidation

### ABSTRACT

The photoreactivity of low molecular camphorquinone (**CQ**) doped in aerated polystyrene matrix was studied. Irradiation at  $\lambda > 380$  nm led mainly to the insertion of one oxygen atom between the carbonyl groups of camphorquinone (**CQ**) and to the formation of camphoric anhydride (**6**). Minor products were cyclopentenecarboxylic acids (**10a–c**). Participation of the matrix on **CQ** photooxidation was negligible. The mechanism of photoconversion of **CQ** has been suggested.

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### 1. Introduction

Camphorquinone (**CQ**) in the presence of H-atom donors is known to be an effective photoinitiator for curing acrylate- and methacrylate-based dental restorative resins [1–3]. **CQ** photochemistry has been studied extensively [4–14]. The structure of its photoproducts depends on the nature of solvent and atmosphere (Schemes 1 and 2). In oxygen-free solutions of **CQ** in benzene and carbon tetrachloride no detectable transformations occurred [4]. The photoreduction of **CQ** in isopropanol and methanol solution was studied by Monroe et al. [5,6]. The products are *endo*-3-hydroxycamphor (**1a**) and *endo*-2-hydroxyepicamphor (**1b**), plus, in methanol, adducts **2a** and **2b**. In toluene or *p*-xylene, 1:1 adducts with solvent molecules (**3a**, **3b**) are the major photoproducts; minor products are hydroxycamphors (**1a**, **1b**) and ring opening products **4a–d** [7–10]. In the absence of oxygen the formation of the most products can be explained by a hydrogen abstraction by excited  $n \rightarrow \pi^*$  triplet state of carbonyl group of **CQ** producing two primary radicals and subsequent reactions of formed radicals.

Photoreduction (abstraction of hydrogen by excited  $n \rightarrow \pi^*$  triplet state of carbonyl group of **CQ**) is the main step in the efficient curing based on the photopolymerization initiated by **CQ** in the presence of alkylamino groups [1,2]. In the presence of oxygen, aforementioned photooxidation reactions are also important [2].

Photochemical reactions of **CQ** in the presence of molecular oxygen are much more complex and yield products whose structures depend on the specific nature of the solvent and the presence of

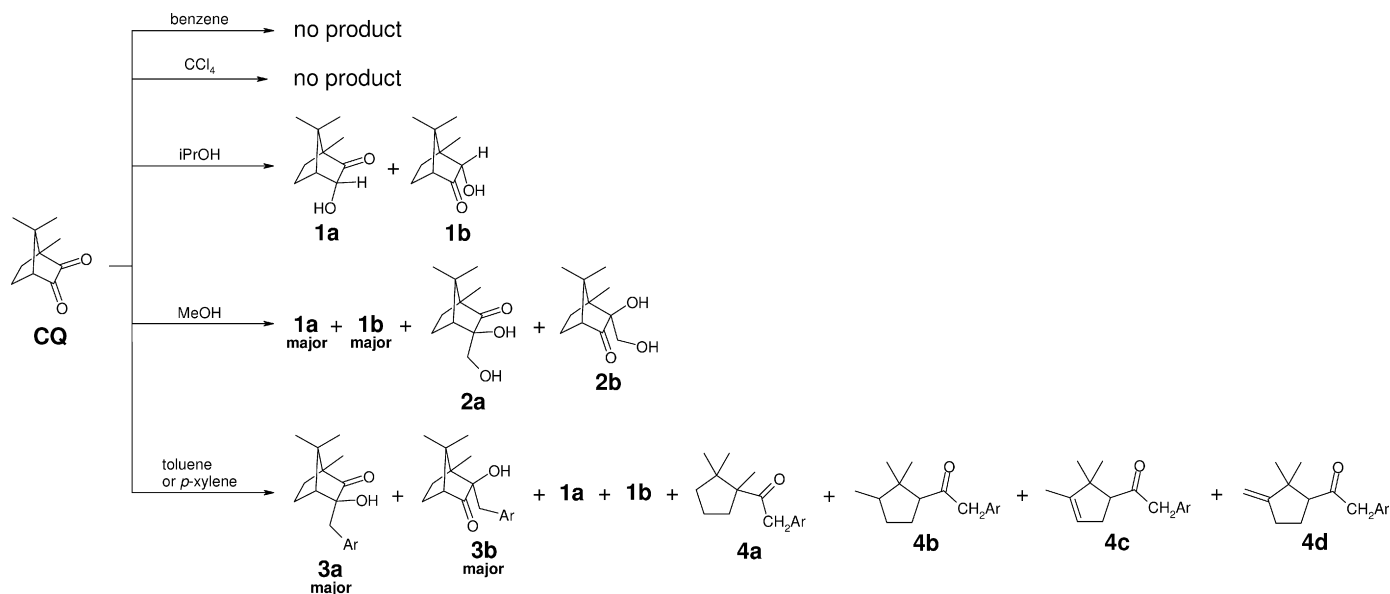
oxygen (Scheme 2). In benzene, camphonolactone (**5a**) and campholytolactone (**5b**) are obtained in largest yield; other products are hydroxycamphors **1a** and **1b**, camphoric anhydride (**6**), camphoric diacid (**7**), and a mixture of other acids [4]. In other solvents lacking easily abstractable hydrogen atoms, such as carbon tetrachloride and *tert*-butanol, **6** is the main photoproduct [4]. In xylene the only products obtained were **6** and **7** [7]. Similarly, irradiation in cyclohexane yielded **6** and **7** [11]. An early investigation by Brett-Salvellsberg reported formation of **6** in ether solution of **CQ** exposed to sunlight [12,13]. According to Meinwald and Klingele, in methanol, the mixture of hydroxycamphors (**1a**, **1b**) and camphoric diacid monoesters (**8a**, **8b**) was formed [4]. These results markedly differ from those obtained by Gream et al. who isolated **6** and **8b** from a reaction carried out under similar condition [11]. Ji et al. published a method for the synthesis of **6** by irradiation of **CQ** in methanol, ethanol or hexane–H<sub>2</sub>O under oxygen atmosphere in 78–85% yields [14]. In anhydrous hexane **6** was not obtained.

Except photoreduction products **1a** and **1b**, the formation of all other products probably has the common intermediate [4,11]. Camphordiacyl peroxide (**9**) (Scheme 2) formed by reaction of  $n \rightarrow \pi^*$  triplet state of carbonyl group of **CQ** and molecular oxygen was presumed to be an intermediate for the formation of lactones [4].

**CQ** irradiated at  $\lambda > 400$  nm in aerated polymer matrix does not yield a stable intramolecular diacyl peroxide (**9**) but camphoric anhydride (**6**) was found [15]. However, irradiation of PS film doped with low molecular benzil (**BZ**) at  $\lambda > 400$  nm (i.e., the long wavelength edge of the  $n \rightarrow \pi^*$  absorption band) led to quantitative formation of benzoyl peroxide [16,17]. Photoperoxidation of polymer bearing covalently bound benzil moieties was used for crosslinking of the polymer and was evaluated as a material for lithographic application [18–23].

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**Scheme 1.** Photochemical reactions of **CQ** in solution under inert atmosphere.

Analogously to **BZ** structures, UV-induced crosslinking may be postulated also with other 1,2-dicarbonyl structures bound to polymer. Therefore, in following paper the polystyrene with pendant **CQ** structures was prepared and its photochemical properties were studied. To understand better the photochemical properties of **CQ** structures bound to polymer chain, prior that, the photochemical study of the low molecular **CQ** in PS was accomplished. The advantage of the low molecular **CQ** model study in comparison with **CQ** bound to polymer is the possibility to separate the products of photooxidation. Therefore, the spectral changes of PS film doped with **CQ** during photooxidation in previous work [15] were extended by the separation and identification of the products by means of NMR and combination of GC and MS in the present work. On the other hand, the elucidation of the nature of photoproducts is also of interest due to the use of **CQ** major in dental materials [24].

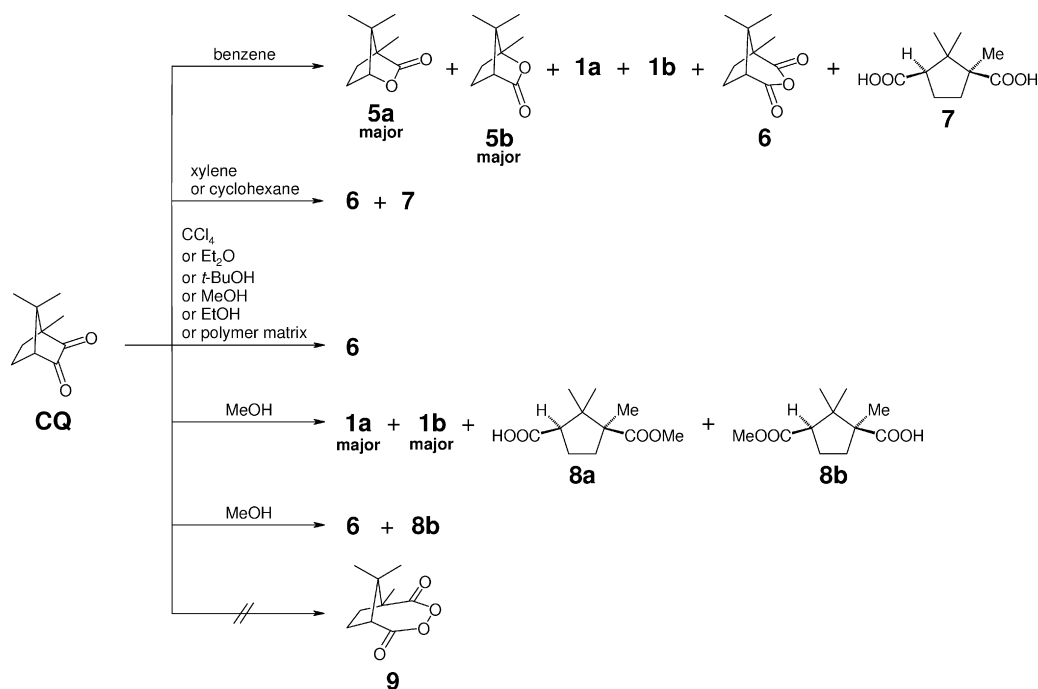
## 2. Materials and methods

### 2.1. Materials

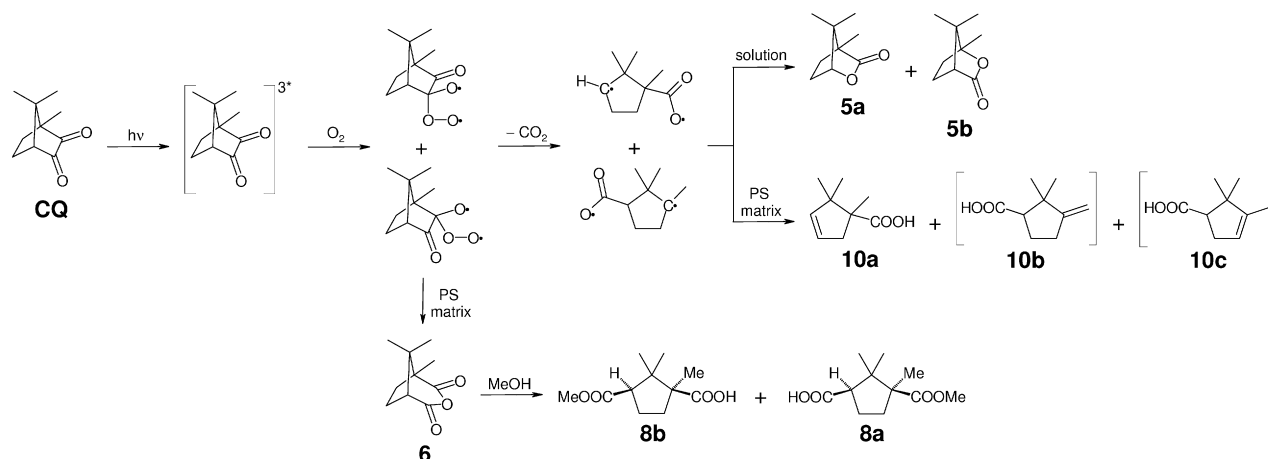
(±)-Camphorquinone (Fluka) was used as received. (±)-Camphoric anhydride (**6**) and (±)-camphoric diacid (**7**) were synthesized according to the previously published procedure [15]. All solvents (p.a.) were redistilled before use.

### 2.2. Characterization

NMR spectra were measured on 600 MHz VNMRS Varian equipped with HCN <sup>13</sup>C enhanced salt tolerant cold probe in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> at 25 °C using the solvent signal as a reference. Chemical shifts are given in the δ-scale (ppm), with coupling constants



**Scheme 2.** Photochemical reactions of **CQ** in solution in presence of molecular oxygen.



Scheme 3. Photooxidation of **CQ** in polystyrene matrix.

$J$  given in Hz. FTIR spectra were recorded on a Nicolet 8700 FT spectrophotometer. GC–MS runs were performed on a Thermo Finnigan Focus GC/DSQ II using a standard capillary column BGB 5 (30 m  $\times$  0.32 mm ID) and applying following standardized temperature profile: 2 min at 110 °C, 10 °C min<sup>-1</sup> until 280 °C, 10 min at 280 °C.

### 2.3. Irradiation

PS (40 mg) films doped with **CQ** (4 mg) with good optical quality about 40  $\mu$ m thick were prepared by casting from 1 mL benzene solutions onto a glass plate (10 cm<sup>2</sup> area). The plate was covered by a Petri dish to slow solvent evaporation. The self-supporting polymer films were separated from the glass by dipping into distilled water. Films were dried to a constant weight at room temperature under vacuum and were irradiated at ambient temperature in air. A homemade “merry-go-round” apparatus was employed. It consisted of a 125 W medium pressure mercury arc placed in a circulating-water-jacketed quartz tube which was surrounded by a 1 cm-thick layer of a liquid filter (500 g NaBr and 3 g Pb(NO<sub>3</sub>)<sub>2</sub> per 1000 mL aqueous solution) transmitting at  $\lambda > 330$  nm. The distance of each sample (placed in rotating eight-rectangular holders) from arc was about 8 cm. Finally, a plastic filter UV CL SR HPR (LLumar, USA) transmitting at  $\lambda > 380$  nm was placed in front of the sample.

### 2.4. Photooxidation of **CQ** in PS

PS film doped with low-molecular **CQ** (10 wt%) was irradiated in air for 7 h to about 80% **CQ** conversion and consequently precipitated from chloroform into methanol. The soluble part was analyzed by GC–MS.

Alternatively six PS films doped with **CQ** (10 wt%) were irradiated for 20 h in air to almost complete **CQ** conversion. NMR spectra were measured directly from irradiated film dissolved in deuteriochloroform, and also from chromatographic fractions of soluble part after precipitation from chloroform into methanol. Concentrated soluble part (20 mg) was separated on a TLC plate (20 cm  $\times$  20 cm). After the first elution with chloroform, the TLC plate was cut off below the spot with  $R_f = 0.53$ . The spot with  $R_f = 0.53$  was extracted with methanol and concentrated at room temperature under reduced pressure. In this fraction beside camphoric anhydride (**6**), camphoric diacid monomethylester (**8b**) was identified by means of <sup>1</sup>H NMR, <sup>13</sup>C NMR and GC–MS. Second elution of the rest of the plate was done with chloroform/acetone 20:1 and the fraction with  $R_f = 0.19$  was separated. Product from silica gel was extracted with methanol and the extract was concentrated at

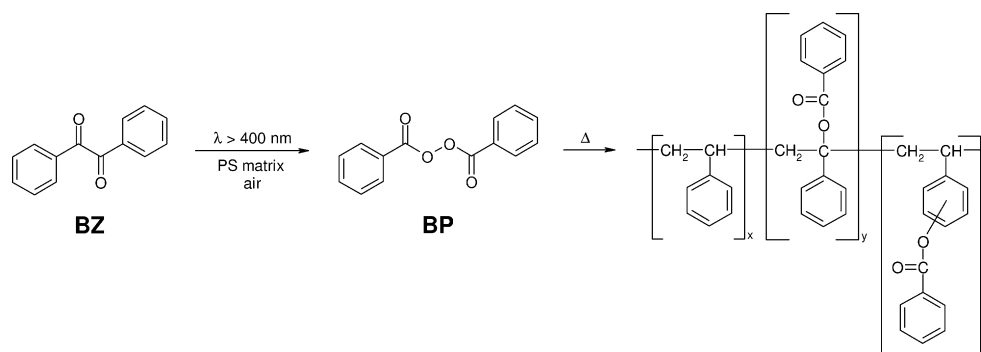
room temperature under reduced pressure. In this fraction 1,2,2-trimethylcyclopent-3-ene-1-carboxylic acid (**10a**) was identified by means of <sup>1</sup>H NMR, <sup>13</sup>C NMR, and GC–MS. Spectral data for **6**, **7**, **8b**, and **10a** are presented in Supplementary information S1.

## 3. Results and discussion

After irradiation of PS film doped with **CQ** at  $\lambda > 380$  nm in air, in FTIR spectra the bands of 1,2-dicarbonyl group of **CQ** (1773, 1756 cm<sup>-1</sup>) decreased quantitatively, hereby this decrease is accompanied by an apparition of the bands at 1810 and 1766 cm<sup>-1</sup> assigned to camphoric anhydride (**6**) as it was clearly reported previously [15]. However, the absorption appearing at 1700 cm<sup>-1</sup> cannot be assigned to camphoric diacid (**7**) as it was assigned earlier [15] since no peak corresponding to authentic sample of **7** was present in NMR spectra of irradiated PS film doped with low molecular **CQ** (10 wt%) dissolved in deuteriochloroform. The major product was **6** only. In <sup>13</sup>C NMR spectrum all signals of **6** are visible and some characteristic peaks are also visible in <sup>1</sup>H NMR spectrum ( $\delta = 2.82, 1.27, 1.09, 0.99$ ); other peaks are overlapped by broad signal of PS aliphatic hydrogens. Some minor photoproducts appeared as well.

By GC–MS analysis (see Supplementary information S2), three peaks with retention times (RT) 7.58, 9.24, and 10.46 min were dominant in GC record and some smaller peaks appeared as well. **CQ** (RT = 7.58 min) and camphoric anhydride **6** (RT = 9.24 min) are unambiguously confirmed by a comparison with the standards. Mass spectrum of a peak at 10.46 min is only slightly different from camphoric diacid **7**. However, the RT of **7** is 11.30 min. The peak at 10.46 min was identified as camphoric diacid monomethylester **8b**. However, **8b** is not a photoproduct of **CQ** photooxidation since it was not seen in NMR spectra of irradiated PS film doped with **CQ**. Monoester **8b** was formed by a reaction of **6** with methanol after the precipitation of the irradiated film. This was proven by keeping **6** in methanol solution for one week. In <sup>1</sup>H NMR spectrum, four characteristic methyl singlets ( $\delta = 3.70, 1.28, 1.27, 0.87$ ) appeared and have the same chemical shifts as **8b** synthesized by Hronowski and Szarek [25]. In <sup>13</sup>C NMR spectrum eleven peaks appeared. Along with **8b**, monomethylester **8a** (RT = 10.27 min) was formed with very similar mass spectrum. The ratio **8b**:**8a** was estimated to be 5:1 by means of GC.

Peak at 5.74 min contains molecular peak at  $m/z = 154$  corresponding to acid **10a** (Scheme 3). Mass fragmentation scheme for **10a** is available in Supplementary information S3. This photoproduct was isolated by TLC. Its structure was elucidated by NMR and confirmed by comparison with published spectroscopic data



**Scheme 4.** Photoperoxidation of **BZ** in aerated glassy PS matrix followed by formation of polystyrene benzoate.

[26,27]. The ratio **6**:**10a** was estimated to be 4:1 by means of NMR. The isomer **10c** at 6.21 min with similar MS spectrum to **10a** was found too. After splitting of three methyl groups the fragment at  $m/z = 111$  prefers the structure **10c** and not **10b**. There are probably common biradical intermediates for the formation of lactones **5a** and **5b** formed in solution [4] as well as for acids **10a–c** formed in PS matrix (Scheme 3). In benzene solution the recombination of radicals in biradical intermediate is preferred. In glassy PS matrix the disproportionation of two radicals in biradical accompanied with transfer of small hydrogen atom is favored. PS matrix may represent restriction for the recombination of radicals.

Addition of molecular oxygen to excited triplet state of monocarbonyl and 1,2-dicarbonyl compounds and formation of 1,4-biradical and singlet oxygen was theoretically treated and reviewed [28]. Commonly accepted formation of 1,4-biradical intermediate and distribution of formed products allowed us to draw Scheme 3. Liberated atomic oxygen during formation of **6** may participate in oxidation of **CQ** to **6**.

Irradiation of PS film doped with low molecular **CQ** leads to only slight decrease of molecular weight of PS matrix at high **CQ** concentration. Therefore, photooxidation of **CQ** in PS as described in Scheme 3 proceeds predominantly with negligible participation of the matrix. There was no difference in FTIR spectra of PS film doped with **CQ** after irradiation, thermal treatment and delimitation of low-molecular compounds by precipitation from chloroform into methanol and that of pure PS. This observation is in sharp contrast with irradiation of PS film doped with low molecular **BZ**, where **BZ** is photooxidized to benzoyl peroxide and consequently decomposed thermally to benzoyloxy radicals which react with the polymer chain [16,17]. As referred earlier [20], very rapid addition of acyloxy radicals to aromatic structures favor the formation of aromatic esters. After precipitation, polystyrene benzoate was obtained (Scheme 4) [29]. The observed differences exclude the formation of diacylperoxide (**9**) and subsequent homolysis to acyloxyradicals in photooxidation of **CQ** in PS matrix.

Present photooxidation of **CQ** in PS matrix mimics the fate of **CQ** photoinitiator in the surface layers of the dental resins composites cured by UV light. Potentially, photopolymers are known to release residual monomers, photoinitiators and similar products resulting from decomposition processes into the environment. For this reason the cytotoxicity of these chemicals is an important issue. The influence of **CQ** and its main photoproduct **6** on human body has been treated [30,31]. Possibly released small concentrations of **6** and **CQ** do not represent health hazard. Cyclopentenecarboxylic acids (**10a–c**) do not contain any moieties indicating toxic behavior at all. Also the influence of “post-curing” on the final properties of the material is important. Since polymer matrix does not participate in **CQ** photooxidation, the “post-curing” of **CQ** alone does not influence final mechanical properties.

## 4. Conclusions

Photooxidation of low molecular **CQ** doped in PS matrix on air by a light with  $\lambda > 380$  nm led to the formation of camphoric anhydride (**6**) as a main photoproduct. Cyclopentenecarboxylic acids (**10a–c**) were formed in lower extent after. Separation and identification of photoproducts by means of GC-MS facilitate understanding the reactions occurring during photooxidation of **CQ** in polymer matrices. Participation of the matrix on **CQ** photooxidation was negligible.

## Acknowledgements

This publication is the result of the project implementation: Centre for materials, layers and systems for applications and chemical processes under extreme conditions Stage II supported by the Research & Development Operational Programme funded by the ERDF. Financial support from grants VEGA 2/0072/11, VEGA 2/0074/10 and APVV-0562-07 is gratefully acknowledged. Authors sincerely thank Mr. Michael Ghobrial for GC-MS measurements and Dr. Slavka Bekešová for their interpretation.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.08.017.

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