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The 2-benzoyl xanthone/triethylamine system as a type **II** photoinitiator: A laser flash photolysis and computational study [1]

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ABSTRACT

2-Benzoylxanthone (**BzX**) was synthesized, characterized and used as type II photoinitiator (**PI**) in combination with triethylamine for the polymerization of methylmethacrylate (**MMA**). The photophysical/photochemical behaviour of the photoinitiator, the involved excited state and the reaction with the amine co-initiator was studied by means of absorption and nanosecond time-resolved absorption spectroscopy. Upon irradiation with 266 or 355 nm laser light, the triplet state ^{3}**BzX*** (λ_{max} = 355 nm and 530 nm) was generated as the only transient (lifetime of 22.7 μs) in nitrogen saturated MeCN solution. ^{3}**BzX*** was confirmed through quenching experiments with oxygen, 2-methylbutadiene, perylene and **MMA** and spectral similarity to benzophenone triplet (^{3}**BP***). The quantum yield of its formation ($\Phi_T = 0.8$) and the molar absorption coefficient ($\varepsilon = 7500\ \mathrm{L\ mol^{-1}\ cm^{-1}}$) was measured in MeCN. The triplet was photoreduced by triethylamine (TEA) *via* photoinduced electron/proton transfer giving the corresponding ketyl and α-amino ethyl radical ($^\bullet$CHMe–NEt$_2$). From the reduction potential of **BzX** measured *via* cyclic voltametry (two cathodic peaks at −1.63 V and −1.91 V vs. Ag/AgCl), an exergonic electron transfer reaction results. The ketyl radical resembles the well-known benzophenone ketyl. In conclusion, the triplet ^{3}**BzX*** corresponds to an n → π* transition localized on the benzoyl substituent and resembles the benzophenone triplet ^{3}**BP*** but deviates from the triplet state of xanthone (^{3}**X***). This is supported through DFT/B3LYP calculations, *viz.*, (i) fully ground and triplet state geometry optimizations show that charge and spin densities are localized on the benzoyl group, and (ii) calculation of the electronic transitions *via* TD-DFT at B3LYP/631G+(d) and PB1BPE/631G+(d) levels of theory shows the local character. Agreement with experiment is better by applying the conductor like polarized continuum model (CPCM) to consider the solvent effect (MeCN).

The effectiveness of **BzX** as photoinitiator for the polymerization of **MMA** is found to be double that of the unsubstituted xanthone (**X**). The photopolymerization rates (R_p) were found to be $7.06 \times 10^{-4}\ \mathrm{mol\ L^{-1}\ s^{-1}}$ in the case of **BzX** and $3.04 \times 10^{-4}\ \mathrm{mol\ L^{-1}\ s^{-1}}$ in the case of **BX**. This is attributed to the fact that triplet ^{3}**BzX*** behaves like the benzophenone triplet ^{3}**BP*** and deviates from that of ^{3}**X***, i.e., it is the localization of the triplet excitation on the benzoyl subunit which renders **BzX** a good type-**II** photoinitiator.

1. Introduction

Photoinitiated polymerization is one of the most rapidly expanding processes because of its widespread applications in printing inks, adhesives, surface coating, microelectronics, printing plates, etc. [1–9]. A crucial component in all photopolymerization systems is the photoinitiator (**PI**) which absorbs light and generates the active radicals to initiate the polymerization. From the mechanistic point of view, there are two main categories of photoinitiators. Type **I** photoinitiators, which undergo direct photofragmentation upon absorption of light and afford radicals capable of inducing polymerization (e.g. benzoin ethers, acylphosphine oxides, hydroxyalkylphenyl ketones, dialkoxy acetophenones, alkyl amino ketones, sulfonyl ketones, silicon derivatives of ketones, etc.), and type **II** photoinitiating systems which are based on hydrogen transfer or electron transfer followed by proton transfer. The latter process takes place between the triplet excited state of the **PI** (usually an aromatic ketone, e.g., benzophenone and thioxanthone) and a coinitiator acting as hydrogen or electron/proton donor (e.g., a thiol or an amine), thereby producing the initiating radicals. Some of the properties needed to improve **PI** efficiency are high absorption coefficients, inefficient quenching of the relevant excited states by the monomer or oxygen and high quantum yields in producing the initiating radicals.

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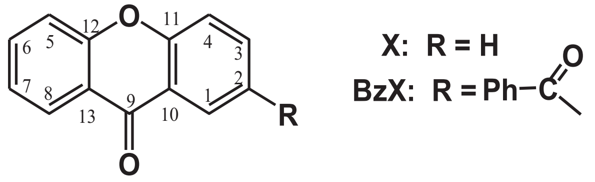

Scheme 1.

Consequently, the role of the photoinitiator efficiency is very crucial and therefore the search for novel compounds that can be used as photoinitiators has continuously received considerable attention in the last three decades. In order to improve the photoinitiator properties some aspects of these studies are focused in replacing the chromophore or in modifying the chromophore through the introduction of suitable substituents (donors or acceptors) on the same chromophore. A variety of substituted benzophenones or thioxanthones have been examined for this purpose and in some cases increased photoinitiation ability was found [10].

Although many substituents in aromatic ketones have been studied, nothing is known regarding the introduction of a second carbonyl group. Thus, in this work we intend to extend the chromophore of xanthone introducing a benzoyl group at the 2-position (**BzX**, Scheme 1), to look for its potential function as photoinitiator and to compare its activity against the unsubstituted xanthone. More precisely, in this work we perform a systematic study which focused: (i) to the photophysical and photochemical properties using steady state absorption/emission and laser flash photolysis techniques, (ii) to compare the photoinitiation activity of the substituted and unsubstituted xanthone (polymerization of **MMA** using **Et_3N** as co-initiator), (iii) to the quenching of the excited state of PIs by triethylamine and monomer (**MMA**), and (iv) to shed light to mechanistic questions related to the specific role played by each carbonyl group. We have also performed quantum mechanical calculations examining the geometry of the ground and triplet excited states, as well as, the relevant molecular orbitals and electronic transitions (PM3, AM1, Ab initio and DFT and TD-DFT) in order to support the interpretation of the obtained results.

The present results show that 2-benzoyl xanthone (**BzX**) functions as a type-**II** photoinitiator with an effectiveness twice as that of the unsubstituted xanthone (**X**) for the polymerization of **MMA**. As the spectral characteristics (photophysical, laser flash photolysis and computational results) indicate, this is attributed to the fact that triplet excitation of **BzX** is localized on the benzoyl subunit rather than on the xanthonyl part. Thus, the triplet **^{3}BzX*** resembles the benzophenone triplet **^{3}BP*** showing inefficient quenching by the monomer **MMA**, undergoing, however, a very competitive electron/proton transfer reaction with the co-initiator **Et_3N** which affords the desired initiating α-aminoethyl radical. In contrast, the quenching of xanthone triplet **^{3}X*** by **MMA** is more competitive compared to the crucial electron transfer step, diminishing thus its polymerization ability.

2. Experimental

2.1. Materials

Acetonotrile, cyclohexane and MeOH (all spectroscopic grades) were obtained from Merck and used without further purification. Xanthone (99%, Aldrich) was recrystallized from ethanol, the triethylamine (TEA, 99%, Aldrich) was distilled under vacuum. Methyl methacrylate (**MMA**, $\geq$99%, Fluka) was washed with 5% aq. NaOH solution, dried over $CaCl_2$ and distilled in vacuum. The 2-benzoylxanthene was prepared according to the previously described procedure [11a]. The preparations were carried out under argon atmosphere using Schlenk techniques. Melting points were taken on a Büchi 510 apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrum GX as KBr pellets. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ solutions on a Brucker AC-250 spectrometer. Chemical shifts (δ) are given in ppm and referenced with respect to the residual signals of the solvent, J values in Hz. Mass spectra were measured on an Agilent 1100 Series LC-MSD-Trap-SL spectrometer.

2.2. Synthesis of 2-benzoyl-xanthone (***BzX***)

A hot ($\sim$80 °C) solution of 0.5 g (1.75 mmol) of 2-benzoylxanthene in 2.5 ml acetic acid was added slowly to a stirred hot solution ($\sim$80 °C) of 1.5 g (5.73 mmol) $Na_2Cr_2O_7$ in 5 ml acetic acid. The mixture was heated at 100 °C for 30 min until the oxidation reaction was completed (checked by TLC). The resulting deeply green solution was left to cool and then hydrolyzed. A greenish-yellow crude solid product was isolated and recrystallized from a mixture of ethanol/chloroform (4:1) giving pale yellow crystals (0.33 g, yield 64%); m.p.: 144–145 °C (lit. [11b] m.p.: 146–147 °C); IR (KBr) (cm^{-1}): 3062 (C–H, Ar), 1660 (C=O, xanthone), 1651 (C=O, ketone), 1605 (C=C, Ar), 1464, 1345, 1316, 1277, 1265 (C–O), 1108, 757, 741; ^{1}H NMR ($CDCl_3$, 250 MHz, 298 K) δ (ppm): 8.70 (1H, d, J = 2 Hz, H_1), 8.31 (1H, dd, J = 8.7, 2 Hz, H_3), 8.28 (1H, dd, J = 8.7, 2 Hz, H_4), 7.78 (2H, dd, *ortho*-H), 7.73 (1H, t, *para*-H), 7.70–7.30 (6H, m, $H_{5,6,7,8}$ and *meta*-H); ^{13}C NMR ($CDCl_3$, 68.9 MHz, 298 K) δ (ppm): 194.9 (C=O), 176.6 (C=O), 158.5 (q), 156.0 (q), 137.2 (q), 135.7, 135.3, 133.2 (q), 132.7, 129.9, 128.9, 128.5, 126.8, 124.6, 121.8 (q), 120.9 (q), 118.8, 118.1; MS (APCI$^+$) m/z: 301.2 [M+H]$^+$, MSMS (ESI$^+$) m/z: 223 (M+-Ph) 104.7 [PhCO$^+$].

2.3. Photopolymerization

Photopolymerizations were carried out in Pyrex tubes ($\lambda > 300$ nm) containing 3 ml of methylmethacrylate and the proper amounts of initiator and triethylamine. They are filled with dry argon prior to irradiation and are placed in a thermostatic bath. An Osram 400 W high pressure lamp was used as light source. At the end of the irradiation the reaction mixture was poured into excess of cold methanol for precipitation. The polymer was isolated by filtration and drying to constant weight in vacuum. The monomer conversions for all samples were determined gravimetrically.

2.4. UV absorption and fluorescence spectroscopy

Absorption spectra were recorded with a UV-vis Hitachi U-2001 spectrophotometer. Fluorescence and excitation spectra were obtained on a Cary Eclipse fluorescence spectrometer at 25 °C.

2.5. Steady-state UV photolyses

The photolyses were performed with a high pressure mercury lamp (400 W) at 20 °C in quartz cuvettes. The photolysis solutions ($\sim$1 mM) were purged with argon or oxygen before irradiation.

2.6. Electrochemistry

Cyclic voltammetric measurements were carried out using a Metrohm instrument, Model 797 VA, Computerace equipped with a three-electrode cell, containing a hanging mercury drop electrode (HMDE) as a working electrode, a platinum wire as an auxiliary electrode and an Ag/AgCl (3.0 mol L^{-1} KCl) reference electrode. The measurements were performed under a nitrogen atmosphere at 25 °C in acetonitrile (ACN, Merck Uvasol reagent grade) containing