

Bicyclic Guanidinium Tetraphenylborate: A Photobase Generator and A Photocatalyst for Living Anionic Ring-Opening Polymerization and Cross-Linking of Polymeric Materials Containing Ester and Hydroxy Groups

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Photobase generators (PBGs) are compounds capable of in situ generating basic species by irradiation (e.g., mostly by UV–vis irradiation). As a photocatalyst for polymer cross-linking and modification, PBGs are widely used in coatings and microelectronics industry, such as photo curing of epoxy resins and photoinduced imidization of poly(amic acid).¹ Thus far, all the reported PBGs produce amines and amidines with pK_a of 10–24 in acetonitrile (AN).² These photogenerated bases, including 1,8-diazabicyclo-undec-7-ene (DBU, $^{AN}pK_a = 24.3$), are not powerful enough to initiate a living ring-opening polymerization (ROP). In comparison, a bicyclic guanidine, namely 1,5,7-triaza-bicyclo [4.4.0]dec-5-ene (TBD), is a stronger base with $^{AN}pK_a$ of 26.03 and has been proved to be a very effective bifunctional catalyst for trans-esterification and ROP of cyclic monomers such as δ -valerolactone (VL) and ϵ -caprolactone (CL). It can simultaneously activate the ester through acyl transfer and trigger the alcohol with hydrogen bonding.³ TBD also catalyzes the reactions between isocyanates with alcohols to form urethanes and the Michael addition of acetoacetates to acrylates,^{3d} which are all suitable base-catalyzed reactions for polymer curing. Therefore, it would be both fundamentally interesting and practically useful to realize PBGs that can generate TBD and other stronger bases for photoinduced living polymerizations and polymer curing.

Herein we propose the photogeneration of TBD from its tetraphenylborate salt (TBD•HBPh₄) via a photoinduced proton transfer reaction. It is known that irradiation of sodium tetraphenylborate (NaBPh₄) can effectively abstract the acidic protons from other molecules, such as water and alcohols.⁴ By comparing pK_a values of TBD, or the acidity of the conjugated acid (TBD•H⁺), with methanol and ethanol ($^{water}pK_a = 13.6$ vs 15.5–16.1),^{2a} it is clear that TBD•H⁺ is a much better proton donor than alcohols. Therefore, TBD•HBPh₄ should be photochemically reactive and able to liberate TBD upon irradiation even in the presence of alcohols and water.

TBD•HBPh₄ was obtained by simply mixing hydrochloric acid (HCl), TBD, and NaBPh₄ in water, followed by filtration and recrystallization.⁵ It appears as white crystalline solids with a melting point at 223 °C and begins to decompose at 243 °C. TBD•HBPh₄ absorbs within the ultraviolet C region (100–280 nm), with an intense peak at 195 nm ($\epsilon_{195nm} = 1.26 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$) and a weak broad peak in 220–280 nm ($\epsilon_{254nm} = 5.05 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$). The target base TBD absorbs weakly at 190–230 nm ($\epsilon_{193nm} = 6.98 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) (Figure 1a).

The base-generating ability of TBD•HBPh₄ was first tested by irradiation of its degassed AN solution at 254 nm, followed by analysis using Phenol Red indicator. The choice of the irradiation wavelength was made for the fact that its absorption coefficient is comparable to those of some widely used photoacid generators, such as arylonium salts and arylsulfonium salts (e.g., 3.0–7.0 \times

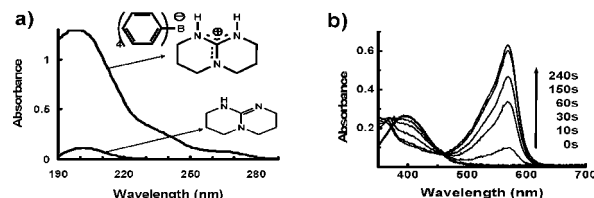


Figure 1. (a) UV–vis absorption spectra of TBD•HBPh₄ and TBD (2.0×10^{-5} M) in AN. (b) Changes of UV–vis spectra of Phenol Red solution upon addition of a solution of TBD•HBPh₄ being irradiated over time.

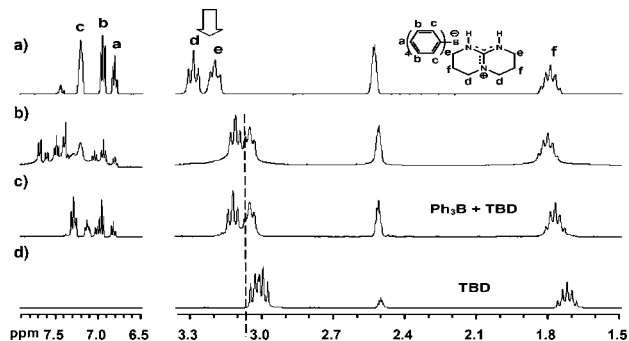
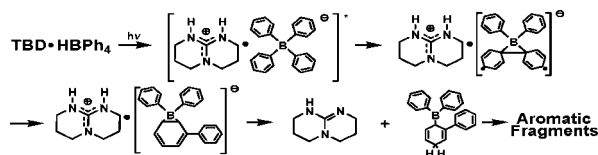


Figure 2. ¹H NMR spectra (DMSO-*d*₆) of TBD•HBPh₄ (a) before and (b) after irradiation at 254 nm with a dose of 92×10^{-6} Einstein, and as well of (c) a mixture of Ph₃B and TBD and (d) TBD.

$10^3 \text{ M}^{-1}\text{cm}^{-1}$ at 250 nm) and this light source is readily available.⁶ Upon addition of irradiated solution of TBD•HBPh₄ to the aqueous solution of Phenol Red, a new band at 560 nm appeared, assigned to the deprotonated Phenol Red after reaction with the released base, and its intensity increased with an increase of irradiation time (Figure 1b). In comparison, TBD or its HCl salt is inert to the photolysis at 254 nm. The photoactivity of TBD•HBPh₄ remains unchanged for at least six months when being stored at room temperature in the dark.

To determine the structures of generated basic species, the course of photolysis of TBD•HBPh₄ with a different amount of dose was monitored by ¹H NMR spectroscopy (see Supporting Information, SI). Protons H_d (3.26 ppm) and H_e (3.16 ppm, Figure 2a) adjacent to the nitrogen atoms in TBD•H⁺ were gradually disappearing and shifting to 3.08 ppm (Figure 2b) after irradiation at 254 nm. In comparison, the same characteristic methylene protons in TBD appeared at 3.01 ppm (Figure 2d). However, since triarylborane is the main product in photolysis of NaBPh₄,^{4a} the in situ formation of an ate-complex between TBD and triarylborane during the photolysis of TBD•HBPh₄ should be expected. Apparently, the ex-situ formed ate-complex displays the same protons at 3.08 ppm (Figure 2c), identical to the in situ formed TBD-Ph₃B complex (Figure 2b). Therefore, the NMR studies confirmed the liberation

Scheme 1. Proposed Mechanism for the Photo-Generation of TBD from TBD•HBPh₄



of TBD from TBD•HBPh₄. Furthermore, by plotting the area of the new peak at 3.08 ppm as a function of absorbed photons, the quantum yield (Φ) for TBD generation is calculated to be 0.18 (SI). A higher efficiency of photolysis of TBD•HBPh₄ can be expected at a shorter wavelength, due to its much higher absorption coefficient.

To investigate the photobase-generating mechanism, the kinetics of photolysis of TBD•HBPh₄ was studied by UV–vis spectroscopy, with reference to the known photochemistry of NaBPh₄ (SI, Figure S9).⁴ Both compounds show nearly identical absorption, suggesting that BPh₄[−] serves as a chromophore rather than the TBD•H⁺ cation. By monitoring the spectral changes during the photolysis of NaBPh₄ and TBD•HBPh₄ under same conditions, the following were observed: (1) a drastic decrease in absorbance at 200 nm and an increase in absorbance at 250 nm with the two tight isosbestic points (192 and 239 nm) for both salts and (2) virtually identical rate constants of photodissociation of $0.0368(\pm 0.002) \text{ s}^{-1}$ and $0.0370(\pm 0.002) \text{ s}^{-1}$ for NaBPh₄ and TBD•HBPh₄, respectively (SI). The results strongly suggest that photolysis of TBD•HBPh₄ proceeds in the same pathway as NaBPh₄. Accordingly, the excited BPh₄[−] ion rearranges and then abstracts a proton from the neighboring TBD•H⁺ cation to release TBD (Scheme 1). The resulting trivalent arylborane further decomposes to aromatic fragments. Considering the higher absorption coefficients in the deep UV region of BPh₄[−] (Figure 1a), TBD can be photogenerated below 200 nm, for example, at 193 nm from ArF excimer laser, in a higher quantum yield than being done at 254 nm. There are clear advantages of using sub-200 nm light in photolithography and other photoinduced processes.⁷

This photobase-generating mechanism implies that other stronger organic bases can be converted to photobases as their HBPh₄ salts. Indeed, photolysis of *t*-BuP₁(dma)•HBPh₄ at 254 nm generated a P₁ base, *t*-butyliminotris(dimethylamino)phosphorane ($^{\Delta n}\text{p}K_a = 26.9$), as verified by ³¹P NMR spectroscopy and pH indicator (SI, Figures S11–S12).

Because TBD can still be released in the presence of alcohols (methanol and ethanol), due to its lower $\text{p}K_a$ than alcohols, TBD•HBPh₄ can be utilized as a photocatalyst for some base-catalyzed reactions such as the anionic ROP of cyclic esters. Thus, bulk polymerization of CL was attempted using 1 mol % of TBD•HBPh₄ in the presence of 1 mol % of *n*-hexanol as an initiator. After irradiation for 5 min at 254 nm in argon, polymerization then proceeded for 8 h at 60 °C. Poly(CL) in a molecular weight (M_n) of $16\,537 \text{ g mol}^{-1}$ or DP of 144 was obtained with ~70% monomer conversion. The ROP rate increased with longer irradiation time (SI, Figure S5a), indicating the release of more base catalysts. The living nature of this ROP is evident by the observed linear relationship between the monomer conversion and molecular weight of poly(CL) (SI, Figure S5b, c). No poly(CL) was formed using NaBPh₄ or Ph₃B, thus eliminating their possible roles as a photocatalyst or in situ generated Lewis catalyst for ROP. It should also be noted that DBU generated from reported PBGs is insufficient to trigger the ROP of CL.^{3b}

Further utilization of TBD•HBPh₄ for photoinduced polymer cross-linking can be envisioned, based on the TBD-catalyzed transesterification reaction between an ester and an alcohol. Thus, upon addition of the irradiated AN solution of TBD•HBPh₄ to a mixture at a 1:1 (wt/wt) ratio of poly(methyl methacrylate) (PMMA) and 2-hydroxyethyl cellulose (HEC) in *N,N*-dimethylformamide, a gel was formed in 30 min at room temperature, indicating polymer cross-linking. This photoinduced polymer cross-linking can also proceed at the interface of the two polymer films. Upon irradiation of a thick film of HEC coated with a thin layer of PMMA containing 5 mol % TBD•HBPh₄, only PMMA on the irradiated areas were left on HEC after washing off the top layer, as evident by a large change in the contact angle of water from 45° (for HEC) to 86° (for PMMA) (SI, Figure S6). Furthermore, a self-photo-cross-linking polymer system can be realized, by introducing a hydroxy-ester moiety in polymer. One example demonstrated herein is the use of hydroxypropyl acrylate (HPA) as a self-cross-linkable unit in the copolymers with methyl methacrylate (MMA) and *N*-vinylpyrrolidone (VP), respectively. Films of the two copolymers, P(MMA-co-HPA) (1:1) and P(VP-co-HPA) (1:1), containing 5 mol % TBD•HBPh₄ were irradiated at 254 nm and then baked at 100 °C for 3 min. Both polymer films became insoluble in organic solvents due to polymer cross-linking, as a result of trans-esterification and subsequent loss of methanol or/and 1,3-propylenediol (SI, Figure S8). In comparison, P(MMA-co-HPA) could not be cross-linked using 5 mol % Ph₃B. Thus, polymers or blends containing hydroxyl and ester groups can be photocross-linked with a catalytic amount of TBD•HBPh₄.

In conclusion, TBD•HBPh₄ represents a new family of short-wave UV PBGs and is able to generate a base 100 times more basic than the strongest base (DBU) generated among all the previously reported PBGs. This PBG enables the photoinduced living ROP of cyclic esters and the photocross-linking of polymeric materials containing the hydroxyl-ester groups.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supporting Information Available: Synthesis, characterization, kinetic studies, polymerization, and cross-linking. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA802816G