

Photocatalytic dechlorination of PCB 138 using leuco-methylene blue and visible light; reaction conditions and mechanisms

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ABSTRACT

A study of dechlorination of PCB 138, under visible light employing methylene blue (MB) and triethylamine (TEA) in acetonitrile/water has been conducted to investigate the details of the mechanism of dechlorination and to determine the efficiency of the process for this representative congener. Two other amines, N-methyldiethanolamine (MEDA) and (triethanolamine) TEOA also replaced TEA and two other solvents, methanol and ethanol replacing acetonitrile were examined for effects on reaction rates. The results show that PCB 138 can be dechlorinated efficiently in this photocatalytic reaction. Clarifying ambiguities in several previous reports, the reduced form of MB, leuco-methylene blue (LMB) was identified as responsible for the photoreaction with its excited state transferring an electron to PCBs; oxidized LMB (i.e. MB) is reduced back to LMB by the excess amine present. The reaction depends on a cycle driven by the amine as a sacrificial electron donor. MEDA proved to be the most efficient electron donor; apparently in consequence of the most favourable steady state concentration of LMB. Methanol and ethanol may be used to replace acetonitrile with little change in the efficiency of the reaction.

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1. Introduction

Photo-assisted methods are a viable remediation option for polychlorinated biphenyls (PCBs) and are especially attractive when compared to incineration, which not only has high costs but also can produce dioxins and benzofurans, which are more toxic than PCBs [1]. Direct photolysis and indirect dechlorination of PCBs using sensitizers are two approaches to photo-assisted remediation. PCBs absorb wavelengths only shorter than 310 nm and their direct dechlorination under short wavelength (254–300 nm) irradiation in various solvents is well known [2]. Direct dechlorination of PCBs at 254 nm in alkaline 2-propanol is the most efficient photodechlorination method yet reported for PCBs. Alkaline 2-propanol is a unique solvent as it initiates a chain reaction resulting in a high quantum yield. The quantum yield of the reaction for dechlorination of Aroclor 1254 is reported to be as high as >30, which is very promising for developing a practical method for remediation of PCB, e.g. in contaminated soil [3].

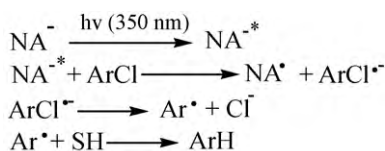
Effective photodechlorination of PCBs at longer wavelengths and possible use of sunlight as the natural irradiation source has also been a topic of considerable interest. Different sensitizers have been used to make use of longer wavelengths to dechlorinate PCBs

[2,4–6]. Among the sensitizers used, those involved in reductive dechlorination of PCBs by a photoinduced electron transfer mechanism are of special interest, because of stepwise dechlorination of PCBs without a danger of producing more toxic (oxygenated) chlorinated compounds. Photoinduced electron transfer methods involve either direct electron transfer from the excited sensitizer (e.g. naphthoxide anion; NA in Scheme 1, Mechanism A) to PCBs [7] or electron transfer from the reagent to the excited state of the PCBs, which is the case for aliphatic amines (Scheme 1, Mechanism B) in a photoredox reaction.

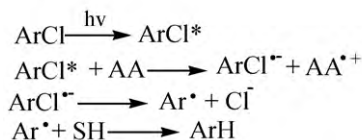
Dye photosensitizers have also been studied for dechlorination of chloroaromatic compounds. Stallard et al. [8] reported a very efficient dye-sensitized photochemical reduction of PCBs using methylene blue (MB) and propane in a potassium hydroxide saturated solution of dimethylformamide under visible light. The mechanism proposed is energy transfer from excited triplet state of MB itself to PCBs, cleavage of C–Cl bond, which produce free radicals that abstract hydrogen from propane molecules. They also included two other alternate mechanisms for dechlorination of PCBs; one involves excited PCB itself which abstract hydrogen from propane molecule and the other is based on a Förster type transfer from the singlet excited state of MB causing C–Cl bond cleavage. In no case the reduced form of the dye, LMB was considered.

Epling et al. [9] used triethylamine along with several dyes under visible light for dechlorination of some chloroaromatic compounds, including 4,4'-dichlorobiphenyl (PCB 15). Methylene blue

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Mechanism B



Scheme 1. Two mechanisms of photoinduced electron transfer; NA: naphthoxide anion; AA: aliphatic amine; ArCl: PCB congener; SH: solvent.

was tested as the sensitizer for dechlorination of PCB 15 in 1:1 acetonitrile:water. The solution was irradiated with a 150 W xenon lamp and 28% of PCB 15 was reduced in 3.5 h. The presence of oxygen was reported to be essential for an efficient reaction (the oxygen role will be discussed later). They considered two different plausible mechanisms for the dechlorination of chloroaromatics. One is based on Tanaka's mechanism [10] which proposes that the excited dye (MB in this mechanism) accepts an electron from amine then the radical anion transfers an electron to the chlorinated compounds. In the other, the excited photosensitizer transfers an electron to aryl radical then it is regenerated by electron transfer from amine. Recognizing limits on their data, they left the actual mechanism of the reaction for further studies. In 2007, Lin and Chang [11] successfully used methylene green along with triethylamine or sodium borohydride for dechlorination of DDT under visible light. No further analysis of mechanism was included in their paper and they mention Tanaka's mechanism (above) as a possibility.

The present study was stimulated by the unresolved mechanistic issues, and our suspicion that excited states of MB itself were not fully able to initiate dechlorination. We study the dechlorination of PCB 138 as a representative higher chlorine PCB using MB and several aliphatic amines under visible light. The mechanism issues raised by Epling et al. [9] will be pursued to show that an important actor has not previously received consideration. As well, the effect of using different amines and different solvents on reaction efficiency will be investigated for possible information of practical use.

2. Material and methods

2.1. Materials

Standard PCB congeners used in this study 2,4'-DiCB (PCB 8), 4,4'-DiCB (PCB 15), 2,4,4'-TriCB (PCB 28), 2,4',5'-TriCB (PCB 31), 3,3',4'-TriCB (PCB 35), 3,4,4'-TriCB (PCB 37), 2,2',3,5'-TetraCB (PCB 44), 2,2',4,5'-TetraCB (PCB 49), 2,3',4,4'-TetraCB (PCB 66), 2,3',4',5'-TetraCB (PCB 70), 3,3',4,4'-TetraCB (PCB 77), 2,2',3,4,5'-PentaCB (PCB 87), 2,2',3,5',6-PentaCB (PCB 95), 2,2',3,4',5'-PentaCB (PCB 97), 2,2',4,4',5-PentaCB (PCB 99), 2,2',4,5,5'-PentaCB (PCB101), 2,3,3',4,4'-PentaCB (PCB 105), 2,3',4,4',5-PentaCB (PCB 118), 2,2',3,4,4',5'-HexaCB (PCB 138) were obtained from Chromatographic Specialties Inc. Methylene blue (Aldrich), triethylamine (Sigma–Aldrich, 99.5%), N-methyldiethanolamine (Aldrich, 99+%), triethanolamine (Fluka, 99.0%), acetonitrile (EMD chemicals, HPLC grade), hexane and methanol (EMD chemicals, ACS reagent grade), ethanol (commercial alcohols, absolute) were used as purchased. Distilled deionized water was used whenever required in the experiments.

2.2. Photolysis procedure, sample and data analyses

A solution containing the desired concentration of PCB 138, methylene blue and aliphatic amine in 10 ml mixed solvent composed of varying amounts of organic solvent (acetonitrile, methanol or ethanol) along with water was prepared in a pyrex tube and deaerated by vigorous bubbling with nitrogen for 10 min before irradiation (variation of times showed 10 min to be effective); the concentration of the reagents and the composition of the solvents used for each experiment are given when reporting the results. The solutions were subjected to irradiation for appropriate times in a Rayonet photoreactor with 14 cool white (except for effect of different aliphatic amines, 7 lamps were used), 8 W (S3b8) visible (fluorescent) lamps. A magnetic bar was used to stir the mixture during irradiation. The intensity of light entering the vials was measured using ferroxilate actinometry, that measures the integrated blue end light up to ~520 nm (it will emerge below why this is the relevant spectral region). The intensity of light entering the vials for different volume of the samples was measured. Intensity decreases proportionally to decreasing volume. Typical intensity of light (for 14 lamps) entering 10 ml of solution was measured to 2.79×10^{16} photons/s. To analyze changes in the solution during irradiation, 0.5 ml aliquots of the PCB solutions were taken at different time intervals and extracted by adding 1 ml of hexane and shaking in a shaker for 15 min. The hexane phase for each sample was analyzed using an Agilent 6890 series gas chromatograph (GC) with an electron capture detector equipped with a DB-608 column (30 m length, 0.25 mm ID, and 0.25 μm film thickness). The GC conditions and the temperature program were chosen as previously reported [12].

2.2.1. Light Emitting Diode (LED) reactors

Two LED reactors, red and blue LEDs, were also used in this study. The internal diameter and height of the reactor are 12.5 cm and 13.5 cm respectively and they are either equipped with 81 Gilway "super bright" (Peabody, MA) E472 blue LEDs or E70 red LEDs (the reactor has been described by Ghosh et al. [13]). The output for the blue LED is centred at 436 nm and for the red LED at ~660 nm. The light intensity entering the 10 ml sample for the blue LED reactor was measured to be 3.23×10^{15} photons/s.

3. Results and discussion

PCB 138 was completely dechlorinated under the visible light (standard fluorescent lamps) in the presence of methylene blue (MB) and triethylamine (TEA), at concentrations chosen to allow TEA to remain in excess over MB, in about 30 min. The decrease in PCB 138 was accompanied by an increase in less chlorinated congeners and biphenyl (BP). Fig. 1 shows the major PCB 138 dechlorination products and their related peak areas under visible light irradiation as a function of time. Based on the retention time of available standards the major peaks were assignable, but there were several unrecognized PCB congeners, which all disappeared after 60 min of irradiation. The final product is biphenyl which reaches an approximate steady state concentration at about 100 min and remains there under irradiation for more than 2.5 h.

3.1. Control experiments

In order to find the effects of MB and TEA individually and the importance of deaeration for the reaction, the results of three corresponding control experiments were compared to a reaction performed in a deaerated solution in the presence of MB and TEA. The results over 1 h of irradiation show that the reaction in the presence of oxygen is slow (only 17% reduction in concentration of PCB 138 compared to >95% in 0.5 h), there is 14% reduction of PCB 138 in

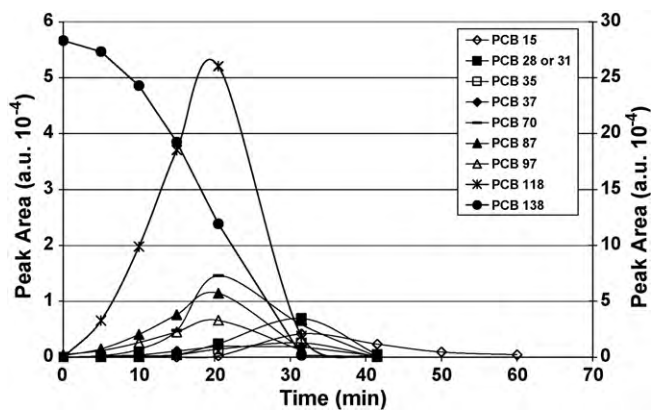


Fig. 1. Dechlorination of PCB138 (6.93×10^{-5} M) using MB (2.09×10^{-3} M) and TEA (0.592 M) and 14 visible lamps in 1:1 acetonitrile–water. Changes for PCB 138 is shown on the second axis.

the absence of MB and no reaction in the absence of TEA, compared to >95% PCB 138 loss in a deaerated solution in the presence of both MB and TEA in 30 min. The limited dechlorination of PCB 138 in the absence of MB could be attributed to the direct reaction of excited PCB 138 with TEA (Mechanism B presented in Section 1). Therefore the presence of TEA along with MB and deaeration of the solution are vital for an efficient reaction. But it has been reported by Epling et al. [9] that to efficiently dechlorinate 4,4'-dichlorobiphenyl (PCB 15) using MB and TEA, the presence of oxygen is essential. To verify that observation, a deaerated solution of PCB 15, MB and TEA, with similar concentrations used by Epling et al. in 1:1 acetonitrile:water was irradiated in the Rayonet with 2 visible lamps. The results show the presence of an induction period (similar to the PCB 138 case, see next section) and 52% reduction in concentration of PCB 15 was observed after 85 min of irradiation. This is more efficient than 3.5 h irradiation of the solution in presence of oxygen reported by Epling et al. [9] irradiating with a 1 kW Xenon arc lamp (This discrepancy with respect to oxygen will be seen below to be important to understanding the mechanism).

3.2. The active role of leuco-MB and mechanism of the reaction

Control experiments show that dechlorination of PCB 138 with TEA under visible light is not efficient and MB itself cannot dechlorinate this congener. When the solutions of PCB 138 along with MB and TEA in 1:1, acetonitrile:water were irradiated with visible light, the GC results showed no change in the concentration of PCB 138 for the first few minutes of the reaction, but the reaction progressed efficiently subsequently. On the other hand visual observations showed that the intense blue colour of the solution starts to disappear as the reaction progress. This qualitative observation is not surprising and the photo-reduction of MB to LMB is well known and well characterized [14,15] (the absorption band of MB in the red region is responsible for this reaction). Presence of an induction period to produce LMB was hypothesized, which was confirmed by performing the experiment at two different light intensities (see the extended induction periods at lower intensity, Fig. 2) and by matching the time required for reduction of MB to LMB in the absence of PCB 138 with the induction period observed.

LMB has a similar structure and oxidation state to phenothiazine (PT). Hawari et al. [6] performed PT-sensitized photodechlorination of Aroclor 1254 at 350 nm. Based on Braun et al.'s 1985 report [16], Hawari et al. [2] argue that the triplet excited state of PT is an efficient electron donor. They suggest that excited PT undergoes ISC (Inter System Crossing) to triplet PT, which then transfers an electron to PCBs. This can be the case for LMB as well. Lee and Mills [17] reported a very reactive, triplet state for LMB with a similar

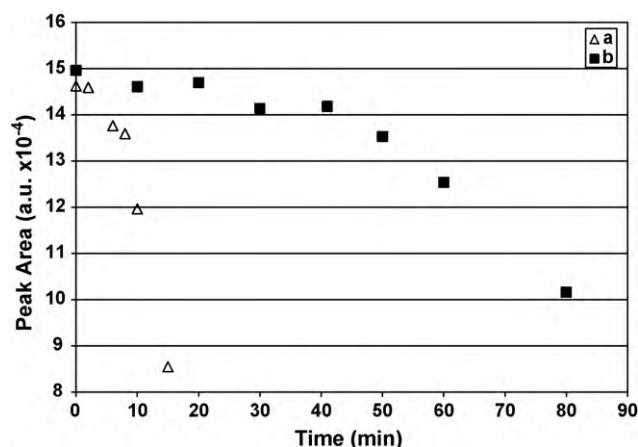


Fig. 2. Degradation of PCB 138 under irradiation with “♦ (a) 14 lamps, ■ (b) 2 lamps”. [PCB] = $\sim 5.59 \times 10^{-5}$ M, [MB] = 2.09×10^{-3} M and [TEA] = 0.592 M in 1:1 ACN:H₂O for both experiments.

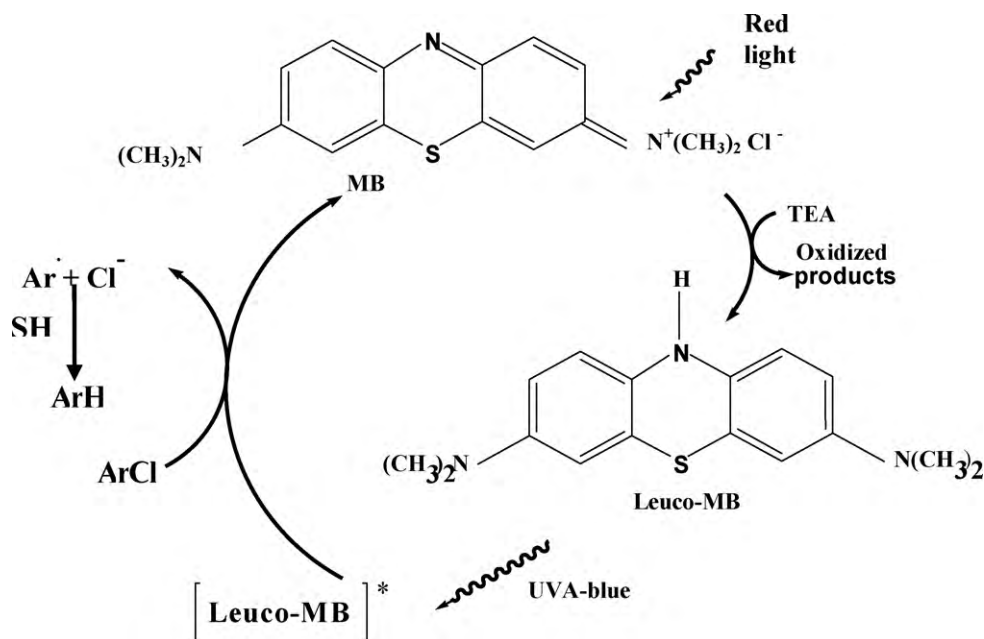
lifetime to triplet MB itself. Therefore an active role for the LMB is proposed. But, what wavelength is required to excite LMB?

The absorption spectrum of LMB shows one weak band in the near-UV (and a weaker maximum in the blue) range of fluorescent lamp output. This is found to be responsible for the reaction. Performing the reaction with a solution of potassium chromate (1 mM K₂CrO₄ in aqueous solution of 0.22 M Na₂CO₃) as a filter to eliminate the UV part from the irradiation source reduces the reaction rate substantially (Fig. S-1 in supplementary material) thereby demonstrating the importance of the UV output of the lamps.

The following mechanism provides a straightforward mechanism for dechlorination of PCBs in this system (Scheme 2) and can account for all of the previous results that have been variously interpreted.

First MB is excited under the red region of the light source, then triethylamine transfers electrons to the excited MB, which produces an anion and then the anion abstracts a proton from water to produce LMB [14,15]. TEA itself converts to triethylaminoxide. In the presence of O₂, LMB is very readily oxidized back to MB, therefore deaeration of the solution is necessary for maximum efficiency. LMB is excited by absorbing light in the short wavelength region of the light source. Triplet LMB transfers an electron to PCB and oxidises back to MB. MB is reduced back to LMB by the excess TEA present in the solution; TEA is consumed during the reaction as a sacrificial electron donor. Whether the electron transfer from the excited state of LMB to PCBs is thermodynamically allowed can be estimated by comparing the reduction potential of excited state of LMB to the reduction potential of PCBs. The reduction potential of excited state of LMB is not reported in literature but for excited state of PT (PT⁺/PT^{*}) it has been reported to be -2.0 V vs. NHE; -2.25 vs. SCE [18] which is negative enough to transfer electron to PCBs.

To confirm the mechanism of the reaction, a similar experiment was performed using red (660 nm) and blue (436 nm) (LEDs) and PCB 77 (3,3',4,4'-tetraCBP) in the presence of TEA. The results are presented in Fig. 3. There is no reaction when the sample is irradiated in the blue LED reactor alone. However, if the sample is irradiated with the red LED before exposure to blue light, then with the blue LED light source, degradation of PCB 77 is observed. MB is reduced to LMB under red light irradiation, which is observable, and then the actual PCB reaction involving LMB occurs under 436 nm irradiation. The difference between this experiment and irradiation with the broad band visible light from the fluorescent lamps is that the oxidized MB is not reduced back to LMB in the absence of red light, therefore it is not a photocatalytic reaction with respect to MB/LMB and LMB is consumed and reaction is limited.



Scheme 2. Mechanism of the catalytic dechlorination of chlorinated biphenyls (ArCl).

3.3. Effect of concentration of triethylamine on the reaction rate

As it was shown in Section 3.1, presence of the TEA is essential for an efficient reaction. The effect of changes in the concentration of TEA on the reaction rate is shown in Fig. 4(1). The results show that the dechlorination rate is significantly affected by the concentration of TEA; as the concentration of TEA increases the reaction rate increases (the difference is more fully defined in Fig. 4(2)).

The key point is that for the reaction to proceed smoothly a steady state concentration of LMB is required. At higher concentration of amine, the reduction of MB reformed in reaction with a PCB will be faster because the steady state concentration of LMB is higher.

3.4. Effect of choice of aliphatic amines on the reaction

As discussed above, TEA is responsible for reduction of methylene blue to leuco-methylene blue by transferring electrons to the excited MB. To investigate the effect of the sacrificial electron donor on the efficiency of the reaction, the same experiments were

performed using two other amines: triethanolamine (TEOA) and N-methyldiethanolamine (MDEA) with MB in 1:1/acetonitrile:water solution. These two amines were chosen based on their free energy change (ΔG) for photoinduced electron transfer to MB in acetonitrile; the more negative the ΔG , the more thermodynamically feasible the photoinduced electron transfer from electron donor

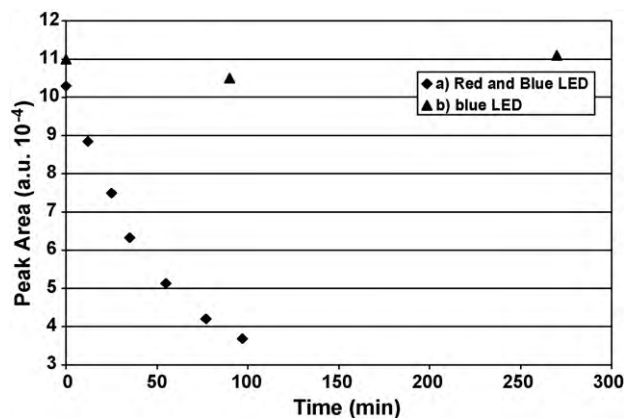


Fig. 3. Dechlorination of PCB 77, 6.22×10^{-5} M, [TEA]=0.652 M, [MB]= 2.23×10^{-3} M in (a) irradiation in the red LED reactor first then in the blue LED; (b) irradiation in the blue LED.

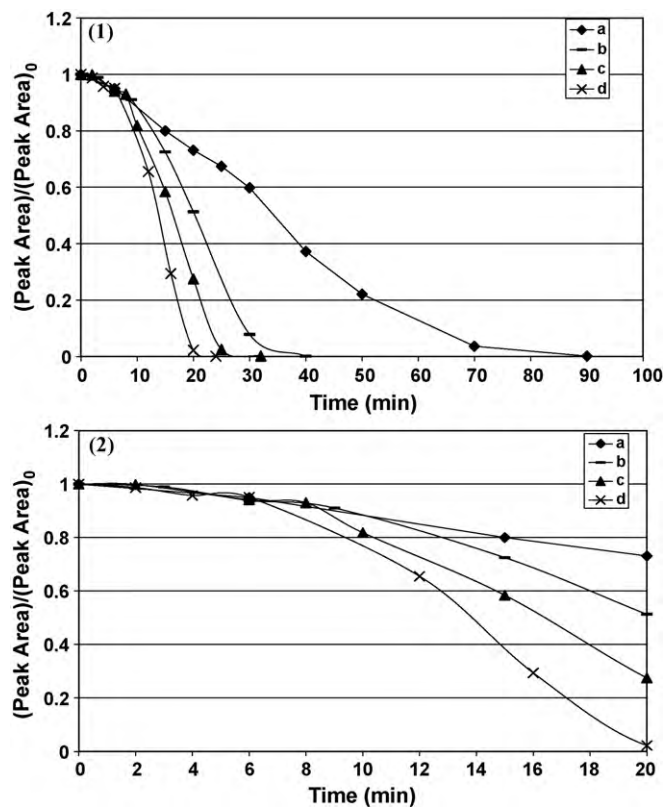


Fig. 4. Dechlorination of PCB 138 (6.55×10^{-5} M) in the presence of MB (2.09×10^{-3} M) and different concentrations of triethylamine: (a) 0.0711 M, (b) 0.358 M, (c) 0.594 M and (d) 0.711 M. The y-axis is the ratio of the peak area at different irradiation times to the peak area at time=0.

Table 1

Effects of aliphatic amines (0.711 M) on the rate of the reaction; [MB] = 2.14×10^{-3} M. k_r is the first order reaction rate constant; irradiation with 7 visible lamps.

Aliphatic amine	[PCB], M	ΔG , kJ/mol ^a	k_r , s ⁻¹	R ²
TEA	4.62×10^{-5}	-14	1.10×10^{-3}	0.9147
TEOA	4.71×10^{-5}	-20	0.48×10^{-3}	0.9623
MDEA	4.71×10^{-5}	-38	3.21×10^{-3}	0.9680

^a ΔG s are for electron transfer from amines to MB.

to MB [19]. In many cases (not all), there is a strong relation between thermodynamic “driving force” and electron transfer rate expressed quantitatively in the well known Marcus equation [20].

The results are presented in Table 1. In order to achieve efficient data “compression”, the reactions are approximated using first order kinetics in PCB applied after the induction period; the data were deconvoluted by starting with the slowest component first. In this case standard kinetic treatments of reactions with induction periods are complicated by the fact that re-oxidation of LMB to MB is the key step and is a photoprocess of complex kinetics. Linear fits yield good R²s and these “apparent” rate constants are useful for qualitative extrapolation of the results to other (possibly practical) configurations; we do not propose that the kinetics are that simple. MDEA was found to be the most efficient amine for dechlorination of PCB 138. A high steady state concentration of LMB is required and MDEA seems to be the best aliphatic amine to rapidly reduce MB back to LMB after it transfers an electron to the PCB (this is also the case at higher concentration of each aliphatic amines, see previous section). In interpreting the data one should be aware of hydrogen bonding of the amine with the solvent which may alter the kinetics of the reaction, perhaps even by changing the reduction potentials [21].

In case of MDEA, the possibility of using lower volume fractions of acetonitrile (20%, 30%) was examined and compared to 1:1 acetonitrile–water. The results show that the reaction in 1:1 acetonitrile–water has the highest rate and 30% acetonitrile is the lowest percent volume of acetonitrile which can be used.

3.5. Effect of solvent on the efficiency of the reaction

In order to test replacement of acetonitrile with a less expensive solvent and in order to reduce the amount of organic solvent (green chemistry), more experiments were performed using methanol or ethanol instead of acetonitrile. The results are shown in Table 2; again reactions are treated as first order in PCB after the induction period and they were deconvoluted by starting with the slowest component (the actual kinetics is not that simple). For all three solvents there were solubility problems with the lowest ratio of organic solvent to water which was observable after a few minutes from the start of the experiments.

The results show that acetonitrile can be replaced by methanol or ethanol and a volume ratio as low as 20% for acetonitrile and ethanol can be used without a substantial change on the efficiency

Table 2

Effect of solvent on the rate of the reaction; %V: volume percent of organic solvent to water, k_r is the first order reaction rate constant, irradiation with 14 visible lamps.

[PCB], M	[MB], M	[TEA], M	%V	k_r , s ⁻¹	R ²
4.39×10^{-5}	1.94×10^{-3}	0.5924	9.1% ACN	1.05×10^{-3}	0.9709
4.69×10^{-5}	2.20×10^{-3}	0.5923	20% ACN	2.26×10^{-3}	0.9612
5.22×10^{-5}	2.13×10^{-3}	0.5923	50% ACN	2.34×10^{-3}	0.9720
8.22×10^{-5}	2.18×10^{-3}	0.5923	20% EtOH	2.21×10^{-3}	0.9483
7.94×10^{-5}	2.13×10^{-3}	0.5923	50% EtOH	2.55×10^{-3}	0.9750
7.65×10^{-5}	2.01×10^{-3}	0.5923	20% MeOH	0.67×10^{-3}	0.9952
7.68×10^{-5}	2.11×10^{-3}	0.5923	30% MeOH	1.49×10^{-3}	0.9657
7.42×10^{-5}	2.11×10^{-3}	0.5923	50% MeOH	2.10×10^{-3}	0.9944

of the reaction; in case of MeOH the best results were obtained in its 50:50 mixture with water.

4. Conclusions

A study on mechanism of photocatalytic dechlorination of PCBs using MB as a sensitizer and triethylamine as a sacrificial electron donor under visible light was performed. The results show that the mechanism involves photoinduced electron transfer from excited state of the reduced form of MB (LMB, with a reduction potential similar to excited PT) to PCBs; while the red region of the light is responsible for the reduction of MB and the UVA-blue region for the dechlorination process. If thermal reducing agents are used instead of amines, it would be possible to dechlorinate PCBs with LED light sources with an output in the UVA region. This matter, which might offer important advantages from a practical point of view, is under study in our laboratories.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.05.023.

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