Ultra-Fast Continuous-Flow Photo Degradation of Organic Peroxide Explosives for Their Efficient Conversion into Hydrogen Peroxide and Possible Application

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1 Introduction

Photo degradation techniques were employed for degradation of organic compounds in water environments since the early 1970's [1]. During the past 15 years, photo degradation has gained further interest as an efficient solution for remediation of nitroaromatic explosives such as polycyclic nitramine (CL-20) and monocyclic nitramine (RDX) [2, 3]. The efficiency of photo degradation is related to strong absorbance of UV-radiation by nitro-compounds. In contrast, there has been little investigation into the photo degradation of organic peroxide explosives (OPEs) such as hexamethylene triperoxide diamine (HMTD), triacetone triperoxide (TATP) or other organic peroxide compounds with explosive potential such as methyl ethyl ketone peroxide (MEKP). Obviously, this is connected with absence of chromophore groups in OPE molecules and low absorbance of these compounds at UV range from 220 to 300 nm. In 2006, UK security and counter-terrorism authority thwarted plans to blow up as many as seven transatlantic airlines with home-made liquid bombs using HMTD as a key explosive [4]. The high solubility of OPEs in water was used to mask the presence of concentrated explosives in bottles of soft beverages within the permitted limit of liquids, which could be taken on plane by boarding passengers. The extreme danger of concentrated solutions of OPEs is further exacerbated by their sensitivity to impact, friction and temperature change. Hence there is a strong need for fast identification of OPEs in suspected samples and, more importantly, for their safe conversion into harmless products.

There are only two reports on application of photo degradation for their indirect determination in a form of H$_2$O$_2$ released after decomposition of these OPEs. Parajuli and Miao [5] reported the detection of TATP using 30 min UV irradiation followed by electrochemiluminescent detection. Schulte-Ladbeck et al. [6] reported determination of HMTD and TATP using HPLC with post-column UV irradiation at 254 nm followed by enzymatic reaction and fluorescent detection. Another related study reported on determination of methyl hydroperoxide, ethyl hydroperoxide, tert.-butyl hydroperoxide and di-tert.-butyl peroxide molecules that do not absorb UV light, in a form of H$_2$O$_2$ released after photo degradation in presence of catalyst (horse radish peroxidase, HRP) in a reactor equipped with a 254 nm UV lamp wrapped with 10 m x 0.3 mm I.D. knitted PTFE coil [7]. Even in presence of HRP, photo degradation of di-tert.-butyl peroxide and tert.-butyl hydroperoxide required 2.8 and 4.7 min, respectively, while methyl hydroperoxide and ethyl hydroperoxide did not show any significant degradation. The inefficiency of converting OPEs into H$_2$O$_2$ was briefly mentioned in [6] due to the decomposition of the released H$_2$O$_2$ under UV light, but no further studies were undertaken in this regard. Hydrogen peroxide as the main product of photo degradation of OPEs undergoes further decomposition under UV irradiation releasing reactive oxygen species (ROS) such as hydroxyl (OH) and hydroperoxyl (HOO$^-$) radicals, superoxide (O$_2^{−}$) radical anion as well as less reactive molecular oxygen (O$_2$) [8]. The decomposition of H$_2$O$_2$ by mineral compounds in basic solutions can also lead to formation of highly reactive singlet oxygen ($^1$O$_2$) [9, 10], although no evidence regarding UV decomposition of aqueous H$_2$O$_2$ producing ($^1$O$_2$) species yet been reported. Thus, efficient photo degradation of OPEs does not necessarily provide their desirable conversion in solutions into H$_2$O$_2$. A possible solution of the problem is to stop the photo degradation of the released H$_2$O$_2$ from OPE degradation. Continuous-flow photochemistry is increasingly gaining ground as a method to facilitate various photochemical processes both in the laboratory and at pilot scale as compared to their batch-flow mode [11]. To consider continuous-flow photo degradation as a solution for remediation of OPEs, quantitative efficiency of the photo degradation for a range of OPEs in the shortest possible time with minimal reagent usage needs to be evaluated in terms of degradation products, irradiation time, conversion degree, degradation percentage, wavelength and source of UV radiation.

The aims of this paper were to develop fast and efficient photo degradation of TATP, HMTD and MEKP through investigating photo degradation pathway and conversion of OPEs into safe products, optimisation of irradiation time, wavelength and source
of UV radiation with a focus on its possible application in screening and remediation of OPEs.

2 Results and Discussion

There are currently no data on the photo degradation of OPEs, but literature data on acid degradation of TATP in HCl vapours reported the production of acetone, 1,1-dichloroacetone, 1,1,1-trichloroacetone, diacetonedi pero xide (DADP), 1,3-dichloroacetone, 1,1,3-trichloroacetone, hexachloroacetone and chloroacetone along with H₂O₂ [12]. Therefore, the photo degradation mechanism of TATP, HMTD and MEKP in different UV radiation source was investigated for the first time and conditions for a safe and selective photo degradation of OPEs were optimised. Special attention was paid to the possibility of selective conversion of OPEs into potentially useful H₂O₂.

The key characteristics to be considered for photo degradation are UV absorption spectra of OPEs, H₂O₂ and the tubing material of reactor coil. The absorption spectra of 12.5 µM HMTD, TATP, MEKP and H₂O₂ as well as 20 mm x 10 mm x 1 mm sheet of FEP poly(tetrafluoroethylene-co-hexafluoropropylene) polymer having structure –(CF₂-CF₂)n–(CF₂-C₂F₄)m– are shown in Fig. 1. The OPE molecules have no specific chromophores responsible for significant absorbance of UV light in the range 240–390 nm, so the absorbance range practically significant for photo degradation purposes of OPEs could be limited to a range 200–215 nm. It should be noted that the majority of organic and inorganic substances absorb light in the range 200–215 nm, so it would be difficult to expect selective and efficient degradation. The increased UV absorbance of H₂O₂ below 215 nm as illustrated in Fig. 1, may cause further degradation of released H₂O₂. Finally, while using a coil reactor, a significant amount of UV light in this range could be absorbed by tubing, but not in the case of transparent FEP tubing used in this work.

Three sources of UV light including zinc lamp with maximum emission at 214 nm, mercury lamp with maximum emission at 254 nm and a deuterium lamp with maximum emission at 200 nm were tested for degradation, which was estimated by using sensitive chemiluminescent detection of released H₂O₂. Table 1 shows the molar extinction coefficients of OPEs at different wavelengths.

Under UV radiation, all OPEs and H₂O₂ undergo degradation and conversion. Due to the fact that OPEs undergo conversion to H₂O₂ as well as further degradation into other products (see discussion later) simultaneously under UV light, it is very important to report OPE degradation efficiency and conversion degree separately. The direct photo degradation products of H₂O₂ in aqueous solutions were reported by Liao and Gurol [8] as follows:

\[
\begin{align*}
\text{Initiation/light absorption:} & \quad H_2O_2 + hv \rightarrow 2OH^- \quad (1) \\
\text{Propagation:} & \quad \text{OH}^- + H_2O_2/HOO^- \rightarrow HOO/O_2^- + H_2O \quad (2) \\
& \quad HOO^- + H_2O_2 \rightarrow \text{OH}^- + H_2O + O_2 \quad (3) \\
\text{Termination:} & \quad HOO^- + HOO^- \rightarrow H_2O_2 + O_2 \quad (4)
\end{align*}
\]

The chemiluminescent detection of H₂O₂ will be affected by reaction driven by transition metal catalysts [13] as follows:

\[
\begin{align*}
\text{M}^{n+} + H_2O_2 \rightarrow \text{M}^{(n+1)^+} + \text{OH}^- + \text{OH}^- \quad (5) \\
\text{M}^{(n+1)^+} + O_2^- \rightarrow \text{M}^{n+} + O_2 \quad (6)
\end{align*}
\]

Table 1. Molar extinction coefficients (εₐ, mol⁻¹cm⁻¹) of 12.5 µM OPEs and H₂O₂ at maximum wavelengths of deuterium, zinc and mercury lamps.
As chemiluminescent detector has high sensitivity to OH∙, HO2⁻ and O₂⁻ radicals, while molecular oxygen (O₂) provides very weak response [13], it is obvious from equation 1-3 and 5 that the presence of OH∙, HO2⁻ and O₂⁻ radicals will greatly enhance the chemiluminescent detector response whilst molecular oxygen (O₂) will decrease the response. So, depending on the reactivity (estimated as standard reduction potentials) of the abovementioned degradation products of H₂O₂, the conversion degree (CD) under UV light can take values >1, <1 or =1. In this case the conversion degree can be defined as follows:

\[
CD = \frac{\text{Detector response of known concentration of H}_2\text{O}_2 \text{ when UV turned on}}{\text{Detector response of known concentration of H}_2\text{O}_2 \text{ when UV turned off}}
\]

Hence, CD = 1 indicates no degradation of H₂O₂, its value >1 indicates production of ROS such as OH∙, HO₂⁻ and O₂⁻ [9-10, 12], whilst its value <1 will indicate possibility of production of less reactive molecular oxygen (O₂).

It is clear from Table 1 that the conversion of H₂O₂ will be more significant under deuterium and zinc lamps as compared to the mercury lamp. However, an intense heat (~200°C-290°C) of the sample in the reactor (as construction of used reactors in Supplementary) produced by the deuterium lamp caused complete degradation of the released H₂O₂, resulting in poor conversion degree and lower response and thus restricted further investigation to only zinc and mercury UV sources.

Fig. 2 shows the CD of 1 nM to 5 mM H₂O₂ in aqueous solution under the zinc and mercury UV lamp. From Fig. 2, it is quite remarkable that in this concentration range of H₂O₂, the CDs were very close to 1 (ranging 0.6-0.9) under the mercury lamp whilst such conversion degree could not be achieved under zinc lamp. The low values of CDs with zinc lamp (ranging 0.025-0.4) in Fig. 2 indicated high degree of production of molecular oxygen (O₂) under zinc lamp. To the contrary, the CDs ranged from 0.6 to 0.9 under mercury lamp for the whole concentration range of aqueous H₂O₂ indicated very small yields molecular oxygen (O₂), which means little or no further degradation of H₂O₂. Therefore, the choice of UV source will depend on the objectives of a particular application. In case of safe degradation of OPEs to molecular oxygen, zinc UV source would be the best option. However, in case of simultaneous screening and selective degradation of OPEs to H₂O₂ only, mercury UV source would be the best option. The corresponding data are provided in Supplementary.

Even though the mercury UV source demonstrated the potential for selective conversion of OPEs to H₂O₂, the residence time of OPEs in the UV reactor coil can alter the outcomes of such conversion. FEP tubing of different length with internal diameter 0.254 mm were coiled around the mercury UV lamp and the detector responses were compared for MEKP, TATP or HMTD as shown in Fig. 3. As the residence time increased from 0.19 min to 1.31 min inside the coil reactor, the chemiluminescent response also increased, which meant the production of ROS increased steadily up to 1.31 min in the reactor. At the same time the enhancement of detector response was also due to the catalytic effect of transition metals present in the solution. However, the termination of photo degradation (eqn. 4) as well as the catalytic effects (eqn.6) started from 1.31 min residence time in the UV reactor coil. The complete degradation of 100 µL injection of 97.8 µM H₂O₂ required a residence time > 2.44 min in mercury UV source. Interestingly, the kinetics of photo degradation of OPEs did not follow the same trend as H₂O₂ in Fig. 3. The initial concentrations of H₂O₂ yield from OPE photo degradation may have a significant effect on CD of H₂O₂. The rapid attenuation of the chemiluminescent responses of TATP and HMTD with increased residence time indicated low initial yield of H₂O₂ from their photo degradation. In this regard, the reaction between the intermediate products from photo degradation of OPEs with ROSs from H₂O₂ degradation cannot also be ruled out. To the contrary, the similar trend of MEKP and H₂O₂ responses indicated an initial high yield of H₂O₂ from MEKP photo degradation (please refer to the discussions of mass spectral analyses of MEKP). According to Fig. 3, shorter residence times (from 0.36 min to 0.5 min with corresponding coil lengths 0.58-0.8 m) were the best option for acceptable chemiluminescent responses from all three sources.
The photo degradation pathways of OPEs in the mercury UV source were studied by running OPE standards into a 61 cm reactor coil and turning the UV lamp off and on alternatively. The mass spectra of 100 mg L⁻¹ HMTD standard in Fig. 4A revealed several adducts of the dialdehyde form of HMTD [14] such as [C₆H₁₀O₆N₂+K⁺] at m/z 245.0168, [C₆H₁₀O₆N₂+Na⁺] at m/z 229.0428, [C₆H₁₀O₆N₂+NH₄⁺] at m/z 224.0875, [C₆H₁₀O₆N₂+H⁺] at m/z 207.0610 when UV was turned off. After UV irradiation at 254 nm inside the UV degradation coil for 0.38 min, peaks corresponding to the dimeric form of a HMTD dialdehyde [2M+Na]⁺ at m/z 409.2042, an ammonium adduct at m/z 404.2487, a sodium adduct of molecular HMTD [C₁₂H₂₆O₈+Na⁺] at m/z 321.1517 and an HMTD product lacking two formaldehyde groups [M-(2H₂O₂+C₈H₁₆)+H⁺] [C₁₂H₂₆O₈-(2H₂O₂)+H⁺] at m/z 224.0895 as well as loss of H₂O₂ from the MEKP trimer (C₁₂H₂₆O₈) when UV was turned off. After UV irradiation at 254 nm inside the UV degradation coil, loss of H₂O₂ and C₈H₁₆ from the MEKP trimer was observed at m/z 224.0895 and m/z 207.0863 as well as loss of H₂O₂ from the MEKP trimer was observed at m/z 231.1591. As no other intermediate product ions of MEKP such as [C₄H₉O₃]⁺ at m/z 105.05 as described by DeTata et al. [16] was found in this study, further loss of the remaining O-O bonds from the MEKP trimer and tetramer under the mercury UV photo degradation cannot be ruled out.

TATP was the most unstable amongst the three OPEs in this study and detailed investigations of the mass spectra of TATP are discussed in the supplementary section.
81±0.003 µL/min flow rate. The mass precision was set to 4 decimals with mass tolerance of 5 mg L⁻¹.

The degradation efficiency of the UV reactor coil was calculated by measuring the concentrations of H₂O₂ produced from OPE degradation by constructing a standard curve of H₂O₂ with details provided in the supplementary. In this study, the results indicated that photo degradation efficiencies of the mercury UV coil were 13-20% for HMTD, 16-26% for TATP and 8-12% for MEKP.

4 Conclusion
This study demonstrated continuous-flow photo degradation for safe and selective conversion of three OPEs (HMTD, MEKP and TATP) to H₂O₂ using two different UV radiation sources. The usage of zinc lamp resulted in fast conversion of OPEs to molecular oxygen, while the use of mercury lamp would be preferable for selective conversion of OPEs to H₂O₂ only using a 61 cm long coil reactor coil with 0.38 minute exposure to UV radiation at 254 nm.

The maximum degradation efficiency of 20%, 26% and 12% for HMTD, TATP and MEKP was achieved with mercury lamp that can be used to drastically reduce the runtime of FIA-chemiluminescent analysis to less than 0.5 min and increase its sensitivity down to nanomole level using previously reported approach [17]. Additionally, this photochemical flow conditions can provide efficient remediation of OPEs with 0.6-0.9 conversion degree depending on concentration of OPEs. Importantly, the kinetic nature of the direct photo degradation of H₂O₂ (i.e., UV+H2O2) can also be applied to maximise ROS production particularly for water treatment.

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References

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