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Short Communication

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Ultra-fast continuous-flow photo degradation of organic peroxide explosives for their efficient conversion into hydrogen peroxide and possible application

Parvez Mahbub[a], Richard Wilson [b], Pavel N. Nesterenko*[a]

Abstract: Fast, quantitative and efficient direct photo degradation of organic peroxide explosives (HMTD, MEKP, TATP) using characteristic continuous-flow UV radiation was investigated in aqueous solutions and achieved in less than 30 seconds.

Keywords: Continuous Flow, Photo Degradation, Oreganic Peroxide Explosives

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 methylethyl 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_2O_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_2O_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_2O_2 was briefly mentioned in [6] due to the decomposition of the released H_2O_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 ($OH^{\cdot}$) and hydroperoxyl ($HOO^{\cdot}$) radicals, superoxide ($O_2^{\cdot-}$) radical anion as well as less reactive molecular oxygen (O_2) [8]. The decomposition of H_2O_2 by mineral compounds in basic solutions can also lead to formation of highly reactive singlet oxygen ($^1O_2$) [9, 10], although no evidence regarding UV decomposition of aqueous H_2O_2 producing ($^1O_2$) species yet been reported. Thus, efficient photo degradation of OPEs does not necessarily provide their desirable conversion in solutions into H_2O_2. A possible solution of the problem is to stop the photo degradation of the released H_2O_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, diacetonediperoxide (DADP), 1,3-dichloroacetone, 1,1,3-trichloroacetone, hexachloroacetone and chloroacetone along with H_2O_2 [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 H_2O_2.

The key characteristics to be considered for photo degradation are UV absorption spectra of OPEs, H_2O_2 and the tubing material of reactor coil. The absorption spectra of 12.5 µM HMTD, TATP, MEKP and H_2O_2 as well as 20 mm x 10 mm x 1 mm sheet of FEP poly(tetrafluoroethylene-co-hexaflouropropylene) polymer having structure $–(CF_2\text{-}CF_2)_n–(CF_2\text{-}C_2F_4)_m–$ 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 H_2O_2 below 215 nm as illustrated in Fig. 1, may cause further degradation of released H_2O_2. 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 H_2O_2. Table 1 shows the molar extinction coefficients of OPEs at different wavelengths.

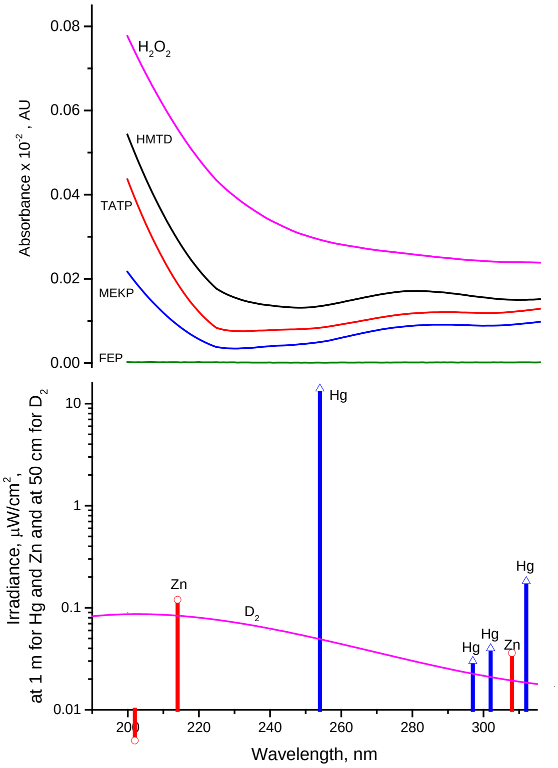

Figure 1. UV absorption spectra of 12.5 µM MEKP, TATP, HMTD and H2O2 aqueous solutions and UV sources including zinc (Zn), mercury (Hg) and deuterium (D_2) lamps.

Under UV radiation, all OPEs and H_2O_2 undergo degradation and conversion. Due to the fact that OPEs undergo conversion to H_2O_2 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 H_2O_2 in aqueous solutions were reported by Liao and Gurol [8] as follows:

Initiation/light absorption

$$H_2O_2 + h\nu \longrightarrow 2OH^{\cdot} \qquad (1)$$

Propagation

$$OH^{\cdot} + H_2O_2/HOO^{-} \longrightarrow HOO^{\cdot}/O_2^{\cdot-} + H_2O \qquad (2)$$

$$HOO^{\cdot} + H_2O_2 \longrightarrow OH^{\cdot} + H_2O + O_2 \qquad (3)$$

Termination

$$HOO^{\cdot} + HOO^{\cdot} \longrightarrow H_2O_2 + O_2 \qquad (4)$$

The chemiluminescent detection of H_2O_2 will be affected by reaction driven by transition metal catalysts [13] as follows:

$$M^{n+} + H_2O_2 \longrightarrow M^{(n+1)+} + OH^{\cdot} + OH^{-} \qquad (5)$$

$$M^{(n+1)+} + O_2^{\cdot-} \longrightarrow M^{n+} + O_2 \qquad (6)$$

Table 1. Molar extinction coefficients (ε_λ, mol^{-1}cm^{-1}) of 12.5 µM OPEs and H_2O_2 at maximum wavelengths of deuterium, zinc and mercury lamps.

Sample	Molar Extinction Coefficients					
	200 nm (D_2)		214 nm (Zn)		254 nm (Hg)	
	ε_λ	$\varepsilon_\lambda/\varepsilon_{200}$	ε_λ	$\varepsilon_\lambda/\varepsilon_{200}$	ε_λ	$\varepsilon_\lambda/\varepsilon_{200}$
MEKP	18	1.00	7	0.38	4	0.22
HMTD	43	1.00	24	0.56	11	0.26
TATP	35	1.00	15	0.43	7	0.20
H_2O_2	62	1.00	45	0.73	23	0.37

As chemiluminescent detector has high sensitivity to $OH^{\cdot}$, $HOO^{\cdot}$ and $O_2^{\cdot -}$ radicals, while molecular oxygen (O_2) provides very weak response [13], it is obvious from equation 1-3 and 5 that the presence of $OH^{\cdot}$, $HOO^{\cdot}$ and $O_2^{\cdot -}$ radicals will greatly enhance the chemiluminescent detector response whilst molecular oxygen (O_2) will decrease the response. So, depending on the reactivity (estimated as standard reduction potentials) of the abovementioned degradation products of H_2O_2, 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:

$$CD = \frac{Detector\ response\ of\ known\ concentration\ of\ H2O2\ when\ UV\ turned\ on}{Detector\ response\ of\ known\ concentration\ of\ H2O2\ when\ UV\ turned\ off} \quad (7)$$

Hence, CD = 1 indicates no degradation of H_2O_2, its value >1 indicates production of ROS such as $OH^{\cdot}$, $HOO^{\cdot}$, $O_2^{\cdot -}$ and $^1O_2$ [9-10, 12], whilst its value <1 will indicate possibility of production of less reactive molecular oxygen (O_2).

It is clear from Table 1 that the conversion of H_2O_2 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 (see construction of used reactors in Supplementary) produced by the deuterium lamp caused complete degradation of the released H_2O_2, 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 H_2O_2 in aqueous solution under the zinc and mercury UV lamp. From Fig. 2, it is quite remarkable that in this concentration range of H_2O_2, 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 (O_2) 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 H_2O_2 indicated very small yields molecular oxygen (O_2), which means little or no further degradation of H_2O_2. 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 H_2O_2 only, mercury UV source would be the best option. The corresponding data are provided in Supplementary.

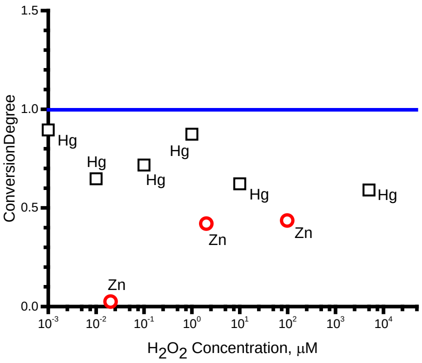

Figure 2. CD of aqueous H_2O_2 under zinc and mercury lamp; Reactor coil length 61 cm; Injection volume 2.2 µL; Flow rate= 81 µL/min. The blue line shows the desired conversion degree of H_2O_2.

Even though the mercury UV source demonstrated the potential for selective conversion of OPEs to H_2O_2, 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 H_2O_2 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 H_2O_2 in Fig. 3. The initial concentrations of H_2O_2 yield from OPE photo degradation may have a significant effect on CD of H_2O_2. The rapid attenuation of the chemiluminescent responses of TATP and HMTD with increased residence time indicated low initial yield of H_2O_2 from their photo degradation. In this regard, the reaction between the intermediate products from photo degradation of OPEs with ROSs from H_2O_2 degradation cannot also be ruled out. To the contrary, the similar trend of MEKP and H_2O_2 responses indicated an initial high yield of H_2O_2 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.

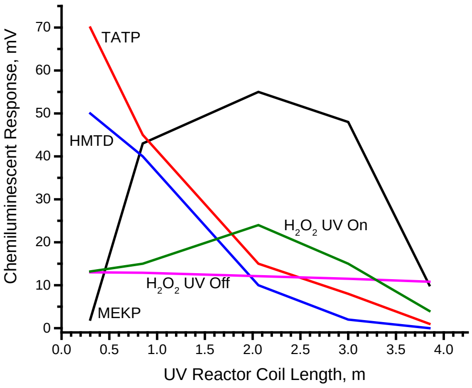

Figure 3. The effect of the coil length on conversion degree shown as the detector response for 100 µL injection of 97.8 µM MEKP, HMTD, TATP and H_2O_2. At 81 µL/min flow rate, the residence time of the sample plug inside the 0.3, 0.85, 2.1, 3.0 and 3.9 m coils were 0.19 min, 0.53 min, 1.31 min, 1.88 min and 2.44 min, respectively.

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 $[C_6H_{10}O_6N_2+K]^+$ at m/z 245.0168, $[C_6H_{10}O_6N_2+Na]^+$ at m/z 229.0428, $[C_6H_{10}O_6N_2+NH_4]^+$ at m/z 224.0875, $[C_6H_{10}O_6N_2+H]^+$ 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 435.0968, a sodium adduct of molecular HMTD $[C_6H_{12}O_6N_2+Na]^+$ at m/z 231.0837 and an HMTD product lacking two formaldehyde groups $[M\text{-}2(CHO)+H]^+$ at m/z 149.0555 were observed. The UV irradiation was strong enough for complete loss of O-O bonds and hence no further peroxide fragments such as $[C_3H_6NO_2]^+$ at m/z 88 and $[C_2H_3NO_2]^+$ at m/z 73 as mentioned in Peña-Quevedo et al. [15] were detected.

The mass spectra in Fig. 5A revealed the existence of sodium adduct of the MEKP tetramer $[C_{16}H_{34}O_{10}+Na]^+$ at m/z 409.2042, an ammonium adduct at m/z 404.2490, as well as several adducts of the MEKP trimer ($C_{12}H_{26}O_8$) when UV was turned off. After UV irradiation at 254 nm inside the UV degradation coil, loss of H_2O_2 and C_8H_{16} from the MEKP tetramer were observed at m/z 224.0895 and m/z 207.0863 as well as loss of H_2O_2 from the MEKP trimer was observed at m/z 231.1591. As no other intermediate product ions of MEKP such as $[C_4H_9O_3]^+$ 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.

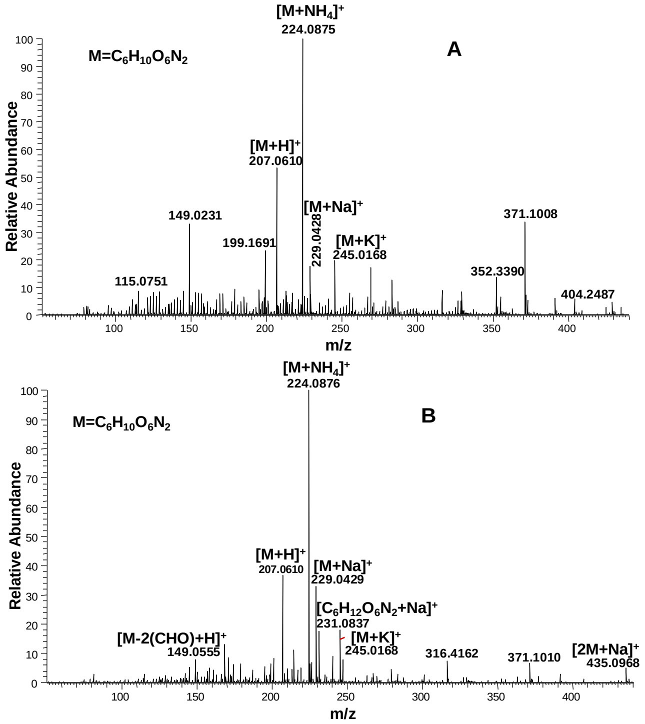

Figure 4. Mass spectra of 100 mg L^{-1} HMTD with UV turned off (A) and UV turned on (B). 10 µL of the HMTD was injected into an Orbitrap mass spectrometer and electrospray ionisation (ESI) with full scan (m/z from 50.00 to 2000.00) were undertaken. Residence time in 61 cm Hg UV coil was 0.38 min at 81±0.003 µL/min flow rate. The mass precision was set to 4 decimals with mass tolerance of 5 mg L^{-1}.

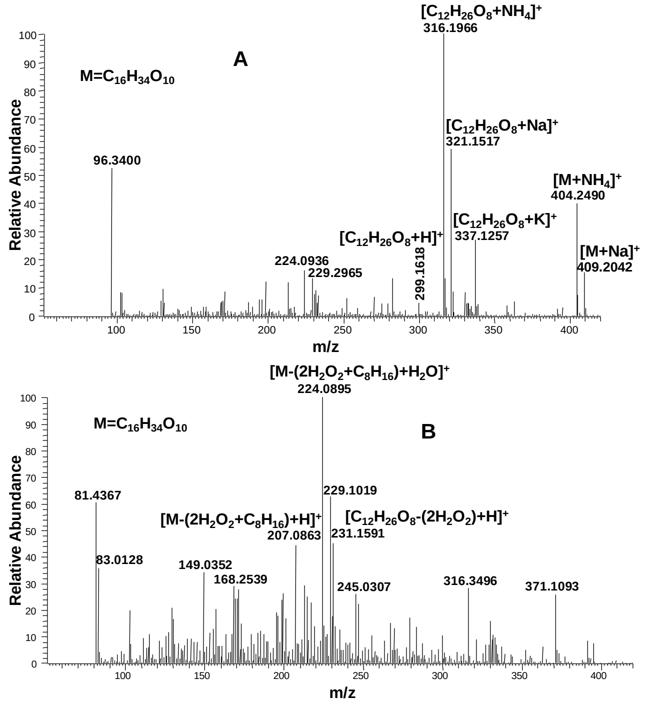

Figure 5. Mass Spectra of 20.5 mg L^{-1} MEKP with UV turned off (A) and UV turned on (B). 10 µL of the MEKP was injected into an Orbitrap mass spectrometer and electrospray ionisation (ESI) with full scan (m/z from 50.00 to 2000.00) were undertaken. Residence time in 61 cm Hg UV coil was 0.38 min at

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 H_2O_2 produced from OPE degradation by constructing a standard curve of H_2O_2 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 H_2O_2 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 H_2O_2 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 H_2O_2 (i.e., UV+H_2O_2) can also be applied to maximise ROS production particularly for water treatment.

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[a] *P. Mahbub, P. N. Nesterenko*
Australian Centre for Research on Separation Science, School of Physical Science
University of Tasmania
Sandy Bay Campus, Hobart 7001 Australia
E-mail: pavel.nesterenko@utas.edu.au

[b] *R. Wilson*
Central Science Laboratory
University of Tasmania
Sandy Bay Campus, Hobart 7001 Australia

Supporting information for this article is available on the WWW under http://www.pep.wiley-vch.de or from the author.

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