

Photo-oxidation of two malonamides, extractant models for minor actinides in nuclear fuel reprocessing

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Abstract

The photo-oxidation of two potential extractants, the *N,N'*-dimethyl, *N,N'*-dibutyl, tetradecyl malonamide (DMDBTDMA) and the *N,N'*-dimethyl, *N,N'*-dibutyl, dodecylethoxy malonamide (DMDBDDEMA) for minor actinides in nuclear fuel reprocessing was followed. The main photoproducts, identified by coupled techniques (GC/FTIR and GC/MS) are malonamides, monoamides and carbonylate derivatives. An irradiation, for 1 h, with a low mercury pressure lamp can destroy initial diamides diluted at 0.075 mol l⁻¹ in *n*-dodecane. With pure solutions of diamides (2.05 mol l⁻¹), destruction needs several hours to be complete. Both diamides only differ by an ether bond, their reactivity under different conditions of photo-oxidation is discussed.

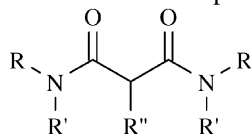
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1. Introduction

To improve the management of radioactive wastes produced after spent nuclear fuel reprocessing, Commissariat à l'Energie Atomique (CEA) developed separation process to separate the minor actinides (Am(III) and Cm(III)) from the high level liquid waste. One separation strategy is based on a two-step process using incinerable extractants (made only with C, H, O, and N atoms). The first step consists of extracting trivalent minor actinides and lanthanides with a diamide (malonamide) molecule, this is the so-called DI-AMEX process.

The semi-developed formula of malonamide is



with R, R' and R'' alkyl or oxyalkyl groups [1–4]. The feasibility of the DIAMEX process has been shown in counter-current “hot” tests with *N,N'*-dimethyl, *N,N'*-dibutyl tetradecyl malonamide (DMDBTDMA; (C₄H₉(CH₃)NCO)₂CH(C₁₄H₂₉)), which was the first reference molecule of the

process [5]. During the extraction process the exposure of the extractant to the hostile environment (concentrated acid, high radiation) lead to its degradation [6]. In order to access the reusability of the extractant, it is necessary to develop cleanup procedure to remove degradation products and remaining metallic cations. After several extraction cycles, the degradation of the solvent imposes its destruction. This study concerns the destruction of the solvent composed by degraded extractant and its degradation product without metallic cations. In a previous study, the thermal destruction in relatively soft conditions of these extractants had been studied, and had shown that bifunctional compounds are decomposed to monofunctional compounds but does not allowed reducing the volume of the solvent [7]. The photo-oxidation seems to be an alternative to the thermal destruction. The photolysis and photo-oxidation of monoamide had been studied and had shown the instability of these molecules [8,9]. The mechanisms of photo-oxidation of polyamides at short and long wavelengths have been studied by Roger et al. [10,11] and shown the same intermediary compounds.

This paper deals with the photo-oxidation of malonamides. Two extractants were compared: the *N,N'*-dimethyl *N,N'*-dibutyl tetradecyl malonamide (DMDBTDMA) and the *N,N'*-dimethyl *N,N'*-dibutyl dodecylethoxyethyl malonamide (DMDBDDEMA; (C₄H₉(CH₃)NCO)₂CH(C₂H₄OC₁₂H₂₅)).

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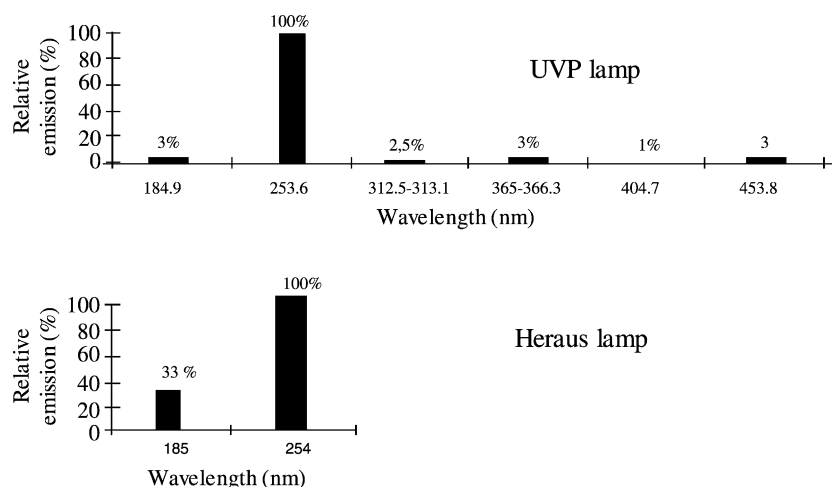


Fig. 1. Main wavelength relative emissions of both UVP and Heraus lamps.

2. Experimental

2.1. Materials

Diamides (purity up to 99%) were synthesised by Panchim (Evry, France). Solutions of diamides were prepared by dilution in pure *n*-dodecane (Acros, 99%). Even if other solvents, such as *n*-hexane and *n*-heptane, present a lower UV absorption, *n*-dodecane was used because of its quite low absorption and a carbon chain length that is in the range of industrial branched aliphatic diluent used in DIAMEX process.

2.2. Devices and photolysis experiments

2.2.1. Lamps

Irradiations were carried out with an UVP Pen-Ray mercury lamp (25 W) or a NIQ 48 Heraus mercury lamp (100 W). Wavelength emissions of these lamps are given in Fig. 1.

2.2.2. Irradiation through a spirale

Diamide solutions were irradiated through a Suprasil quartz spirale (cut-off <200 nm). The circulation of the solution in the spirale was controlled by a Teflon pump as shown in Fig. 2. Due to irradiation and lamp electric power, the solution temperatures reach quickly from room temperature to 45 and 55 °C for UVP and Heraus devices, respectively. For each experiment, the real irradiation time (T_{irr}) was calculated taking in account volumes of initial solution (V_{sol}), spirale (V_{spi}) and samples (V_{samp}) to follow the reaction and the time of the experiment (T_{exp}). The irradiation time is given by the relation:

$$T_{\text{irr}} = T_{\text{exp}} \left(\frac{V_{\text{spi}}}{V_{\text{sol}} - V_{\text{samp}}} \right)$$

Initial volumes V_{sol} were in a range between 10 and 14 ml and V_{samp} was fixed at 50 μl .

2.2.3. Oxidant addition

With the UVP device, molecular oxygen at a flow rate of 2 ml min^{-1} was directly introduced in the studied solution. In another experiments with the same device, hydrogen peroxide or water was introduced regularly (volume of 100 μl after each sampling).

2.2.4. Direct irradiation by immersion of the lamp

Experiments were also carried out with direct immersion of the UVP lamp in diamide solution (17 ml) that was placed in a Pyrex tube (i.d.: 135 mm). The residual absorption by the spirale, and the air between the lamp and the spirale were then suppressed. No circulation of the solution was realised and homogeneity was absolutely not verified. The elevation of temperature solution was measured at 51 °C with the direct immersion of UVP lamp.

2.2.5. Influence of concentration

Solutions of DMDBDTMA at 0.25, 0.075, 0.025 and 0.0075 mol l^{-1} in *n*-dodecane have been tested with Heraus device to follow the influence of concentration.

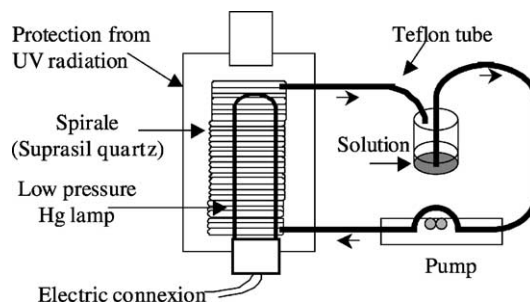


Fig. 2. Device for photo-oxidation.

2.3. Analysis

GC/MS and GC/FTIR were used to separate and to identify photoproducts. GC/FID was used to quantify the major identified compounds. All conditions of separation and detection are described in a previous paper [7].

UV spectra were recorded on a Secomam spectrophotometer, bandwidth 2 nm, scanspeed 1800 nm min⁻¹, 10 mm pathlength quartz cell.

2.4. Destruction indicator

Destruction was followed with an indicator, the global residual percentage (GRP), based on the conversion ratio T_i of the initial diamide into product i taking into account molecular weights. The GRP calculation is given by the relation:

$$\text{GRP} = \sum_i \left(\frac{M_i}{M_d} \right) \times T_i$$

with M_i is the molecular weight of molecule i and M_d the molecular weight of initial diamide, T_i the ratio (moles of molecule i /moles of initial diamide). When T_i was lower than 1%, such a conversion was not included in the calculation.

3. Results and discussion

3.1. Absorbance of diamides

The absorbance of diamide solutions, at 1 mmol l⁻¹ in *n*-dodecane, is given in Fig. 3. Both diamides present a similar absorption for all wavelengths. These spectra show the interest to use lamps with low wavelength emission because diamides absorb UV-radiation lower than 230 nm.

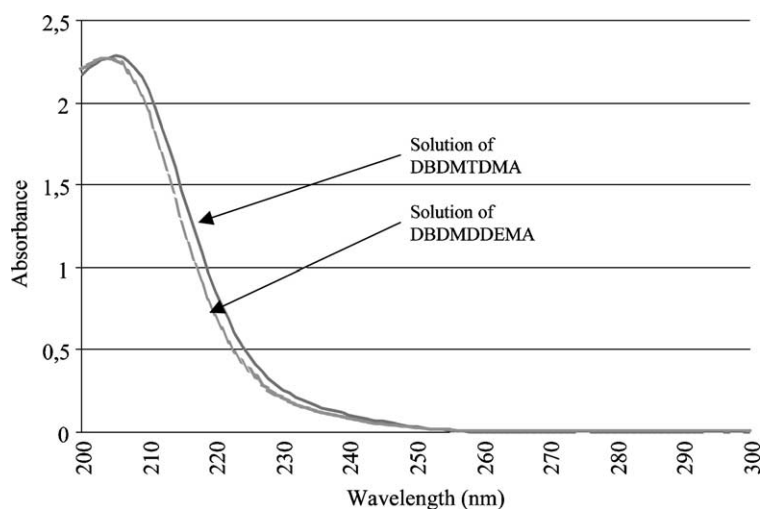


Fig. 3. UV spectra of diamide solutions (1 mmol l⁻¹ in *n*-dodecane, zero absorbance with pure *n*-dodecane) at room temperature.

Table 1
Identified *n*-dodecane photo-products (2:45 h with UVP device and peristaltic pump)

Retention time (s) DB5-MS	Molecular weight (g mol ⁻¹)	Identified structure
417–421	88	1,4-Dioxan
498–502	128	Octanone
506–510	88	Tetrahydro 3-furanol
600–604	142	Nonanone
607–611	156	Undecane
615–619	100	3-Methyl 4-penten-1-ol
674–678	130	Ethyl pentanoate
705–709	158	Decanol
710–720	170	<i>n</i>-Dodecane
797–801	182	Dodecanediol
802–806	182	Dodecenol
812–816	182	Dodecanediol
826–830	182	Cyclododecanone
892–896	184	Dodecanone
907–911	184	Cyclododecanol
929–933	184	Dodecanal
1042–1046	198	Tridecanal or 4-methyl tridecane

Major compounds are written in bold.

3.2. Photo-oxidation of pure *n*-dodecane

Photo-oxidation of pure *n*-dodecane with both UVP and Heraus lamps leads to similar results. For 1 h of irradiation, 12% of *n*-dodecane is degraded and after 2 h, <20% of degradation is observed. After a quite long irradiation time (>6 h), the rate of *n*-dodecane destruction reaches to 30%. This solvent is quite stable and photoproducts are not too reactive (Table 1). Diamide photodegradation studies can be carried out with a minimum of interferences.

3.3. Photo-oxidation of diamides: qualification

Photodegradation of diamides leads to lower malonamides, monoamides but also oxidised compounds such

Table 2
Identification of main photo-products from DMDBTDMA solution in *n*-dodecane

Retention time (s)	Molecular weight (g mol ⁻¹)	Main identified products
180–184	101	<i>N</i> -butyl formamide (BFA)
184–188	115	<i>N</i>-butyl <i>N</i>-methyl formamide (BMFA)
433–437	184	Dodecanone
449–453	184	Cyclododecanol
455–459	184	Dodecanal
536–540	212	Pentadecane
615–619	186	Undecanoic acid
897–901	256	Pentadecanoic acid
1133–1137	297	<i>N</i> -methyl <i>N</i> -propyl hexadecanamide (MPrHDA)
1201–1205	269	<i>N</i> -methyl hexadecanamide (MHDA)
1228–1232	325	H(C ₃ H ₇ CO)NCOC ₁₅ H ₃₁ (Imide)
1311–1325	311	<i>N</i> -butyl hexadecanamide (BHDA)
1409–1413	325	<i>N</i>-butyl <i>N</i>-methyl hexadecanamide (BMHDA)
1466–1470	354	<i>N</i> -butyl tetradecyl malonamide (BTDMA)
1525–1529	368	<i>N</i> -butyl <i>N</i> -methyl tetradecyl malonamide (BMTDMA)
1649–1653	410	<i>N,N'</i>-dibutyl tetradecyl malonamide (DBTDMA)
1742–1746	382	<i>N</i> -butyl <i>N,N'</i> -dimethyl tetradecyl malonamide (BDMTDMA)
1914–1918	424	<i>N,N'</i> -dibutyl <i>N</i> -methyl tetradecyl malonamide (DBMTDMA)
2429–2433	438	<i>N,N'</i> -dimethyl <i>N,N'</i> -dibutyl tetradecyl malonamide (DMDBTDMA)

17:44 h irradiation time with standard conditions, major compounds are written in bold.

aldehydes, ketones and carboxylic acids. Tables 2 and 3 give the lists of by-products from DMDBTDMA and DMDBDDEMA, respectively. For both diamides, bonds in α position of the amide group are easily broken [9]. The hydrogen lability of C _{α} -H leads to cleavages of alkyl bonds (methyl or butyl) on Nitrogen and of C-CO bond. This last cleavage is known as Norrish type I. Norrish type II (cleavage of the neighbour C _{α} -C _{β} bond of carbonyl group) is also observed even if tetradecanoic acid, formed from DMDBTDMA, is not a major compound and not reported in Table 2. No polymerisation reaction was observed. The degradation pathway of DMDBTDMA is shown in Fig. 4.

The alkyl chain with the ether bond allows the specific formation of products from DMDBDDEMA, such as undecanoic, dodecanoic and dodecyloxybutanoic acid. Other compounds are obtained as for DMDBTDMA by cleavage of alkyl groups (methyl or butyl) or C-CO and C-C bonds. All main photoproducts are listed in Table 3. The global photo-degradation pathway is independent to the presence of molecular oxygen, water or hydrogen peroxide because in these different cases, no new by-products were identified.

Table 3
Identification of main photo-products from DMDBDDEMA solution in *n*-dodecane

Retention time (s)	Molecular weight (g mol ⁻¹)	Main identified products
191–195	115	<i>N</i>-butyl <i>N</i>-methyl formamide (BMFA)
343–347	143	<i>N</i> -butyl butanamide (BBA)
368–372	157	<i>N</i> -butyl <i>N</i> -methyl butanamide (BMBA)
434–438	184	Dodecanone
450–454	184	Cyclododecanol
456–460	184	Dodecanal
516–520	196	1-Tetradecene
536–540	201	<i>N</i> -butyl <i>N</i> -methyl ethyl oxy butanamide (BMEOBA)
558–562	198	Tetradecane
581–585	228	Dodecyl oxy propane
617–621	186	Undecanoic acid
660–656	200	Dodecanic acid
848–852	272	Dodecyl oxybutanoic acid
1029–1033	313	<i>N</i> -propyl dodecyl oxy butanamide (PrDDOBA)
1129–1133	271	Dodecyl oxy butanamide (DDOBA)
1229–1233	285	<i>N</i> -methyl dodecyl oxy butanamide (MDDOBA)
1344–1348	327	<i>N</i> -butyl <i>N</i> -methyl undecyl oxy butanamide (BMUOBA)
1416–1420	327	<i>N</i> -butyl dodecyl oxy butanamide (BDDOBA)
1435–1439	341	<i>N</i>-butyl <i>N</i>-methyl dodecyl oxy butanamide (BMDDOBA)
1498–1502	384	<i>N</i> -butyl <i>N</i> -methyl dodecyl ethoxy malonamide (BMDDEMA)
1542–1546	355	(CH ₃)(C ₃ H ₇ CO)NCOC ₃ H ₇ OC ₁₂ H ₂₅ (Imide)
1565–1569	355	(HOC)(C ₄ H ₉)NCOC ₃ H ₇ OC ₁₂ H ₂₅ (Imide)
1677–1681	426	<i>N,N'</i>-dibutyl dodecyl ethoxy malonamide (DBDDEMA)
1793–1797	398	<i>N</i> -butyl <i>N,N'</i> -dimethyl dodecylethoxymalonamide (BDMDEMA)
1845–1849	440	<i>N</i> -butyl <i>N</i> -propyl <i>N,N'</i> -dimethyl dodecylethoxymalonamide (BPrDMDDEMA)
1951–1955	440	<i>N,N'</i> -dimethyl <i>N,N'</i> -dibutyl undecyl ethoxy malonamide (DMDBUDEMA)
2227–2231	440	<i>N</i> -methyl <i>N,N'</i> -dibutyl dodecylethoxymalonamide (MDBDDEMA)
2680–2684	454	<i>N,N'</i>-dimethyl <i>N,N'</i>-dibutyl dodecylethoxymalonamide (DMDBDDEMA)

14:40 h irradiation time with standard conditions, major compounds are written in bold.

Some kinds of amide degradations are known to product carboxylic acids from alkyl chains. Related to this point, such formations were observed after thermal oxidation of substituted malonamides [7] and tertiary amides [12,13] or hydrolysis of diamide [4,14]. Photodegradation of amides was less studied excepted for some polyamides and some amide derivatives [15].

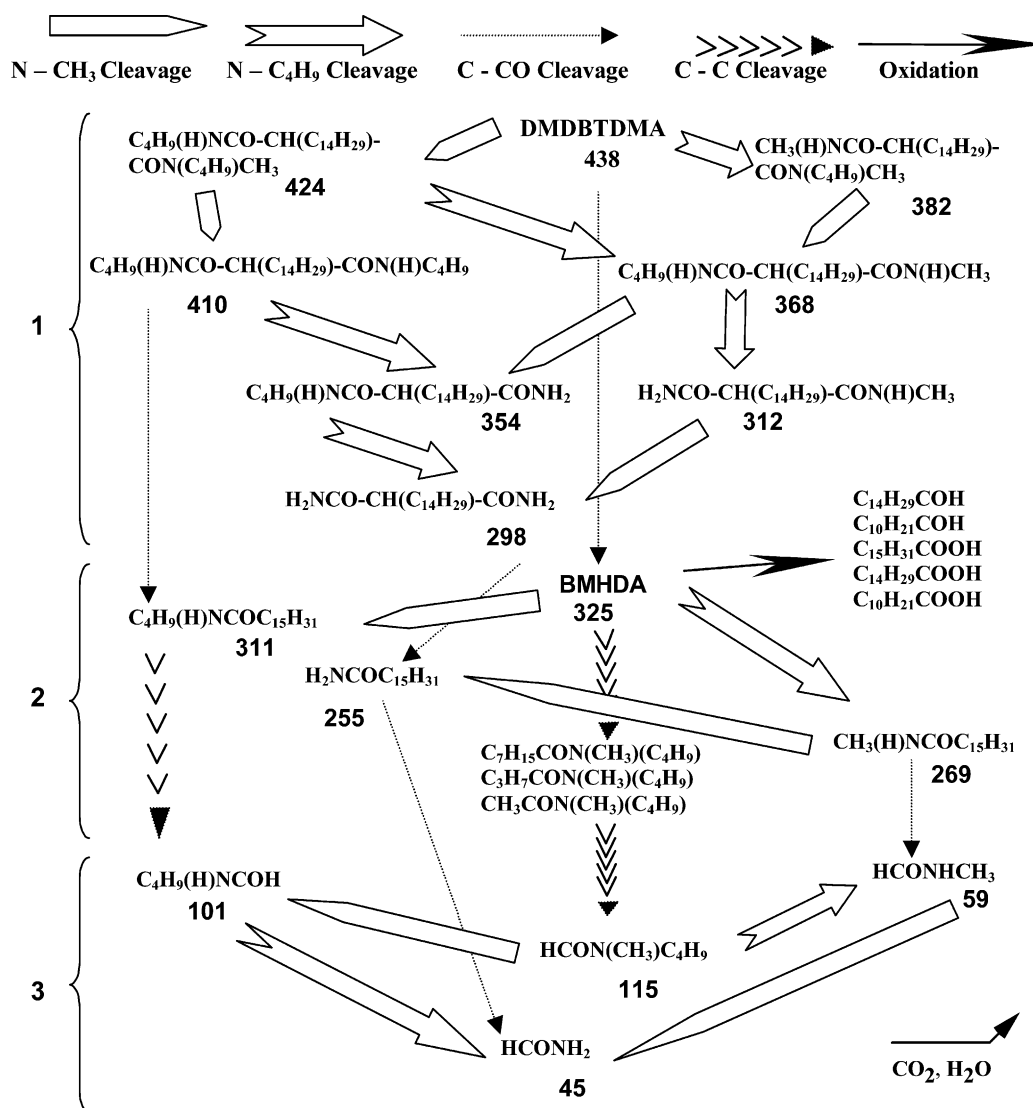


Fig. 4. Experimental photo-degradation pathway for DMDBTDMA (levels 1–3 correspond to malonamides, monoamides and formamides, respectively, that are given with their molecular weight, main oxidation products are placed between levels 1 and 2 on the right of the pathway).

3.4. Photo-oxidation of diamides: quantitation

Looking at residual amounts of both diamides (Fig. 5), the photo-degradation of DMDBDDEMA is less rapid than for DMDBTDMA, in the experimental conditions, even if the presence of an ether bond was susceptible to increase weakness of DMDBDDEMA. But this observation differs when the GRP is followed showing that all by-products with the ether bond are degraded quicker than those without such particularity. Initial diamides follow the same tendency and the difference of residual percentage is around 5%. Photo-products of DMDBDDEMA and especially those formed by the oxoalkyl chain are probably reactive enough to increase the degradation of *n*-dodecane. For both diamides, the main by-products are monoamides that are BMHDA and BMDDOBA for DMDBTDMA and DMDBDDEMA, respectively.

3.4.1. Oxidant addition

No significant modification of DMDBTDMA destruction kinetics was observed by adding molecular oxygen (2 ml min⁻¹), hydrogen peroxide or water (Fig. 6). The presence of molecular oxygen decreases the level of BMHDA. This major compound does not exceed 15% comparatively to 25% without oxidant.

3.4.2. Lamp immersion

With lamp immersion, little gaseous emission was observed around the lamp. The very low quantity of gas did not allow its analysis but can be due to volatile compounds (formed by degradation or photo-oxidation reaction) easily emitted with respect to the temperature of the lamp.

Similar degradation chromatograms of 0.5 mol l⁻¹ solutions were observed with or without the spirale. These results, which are qualitatively similar, indicate that the spirale

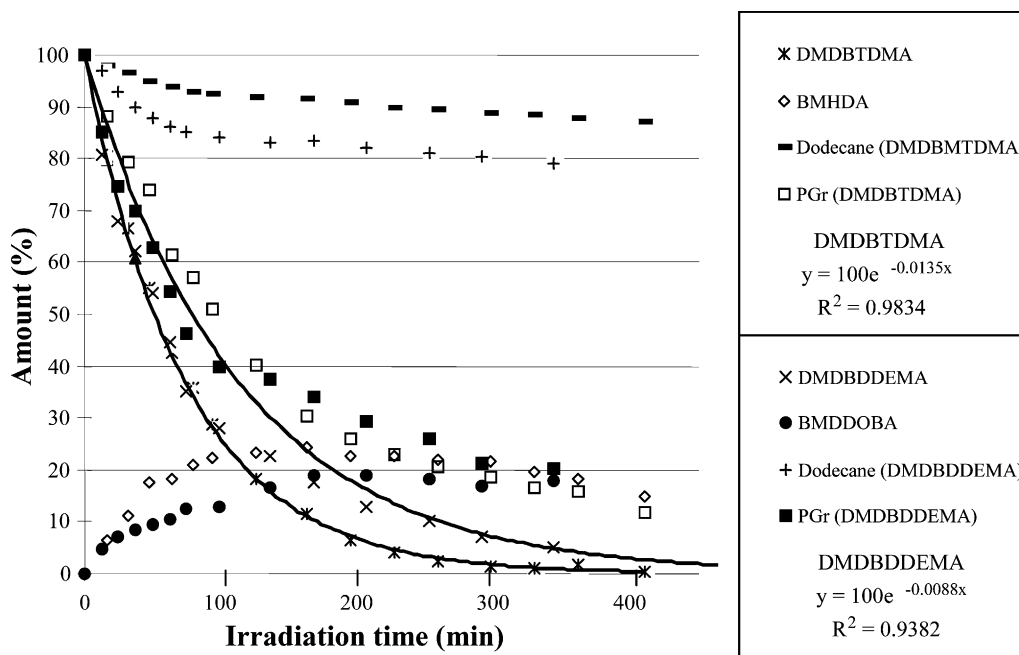


Fig. 5. Photo-oxidation (UVP lamp) of 0.5 mol l^{-1} DMDBTDMA and DMDBDDEMA solutions.

does not cut off active radiations on the diamide. Quantitatively, kinetics seems similar even if the thickness of the irradiated solution are different for both cases.

3.4.3. Influence of dilution

When diluted at 0.5 mol l^{-1} in *n*-dodecane instead of used as pure solution of 2.5 mol l^{-1} , DMDBTDMA is four times quickly degraded. Such correlation between concentration and degradation kinetic indicates that irradiation photonic

flux is a limitant factor because radiations from the lamp are absorbed by a very thin thickness of solution.

3.4.4. Comparison of devices

Degradation efficiency of both lamps (Heraus and UVP) was compared on DMDBTDMA solution as shown in Fig. 7. Degradation kinetic is close to order 1 for both devices even if kinetic constant is a little lower for Heraus than for UVP device. GRP values are close too. The 10°C

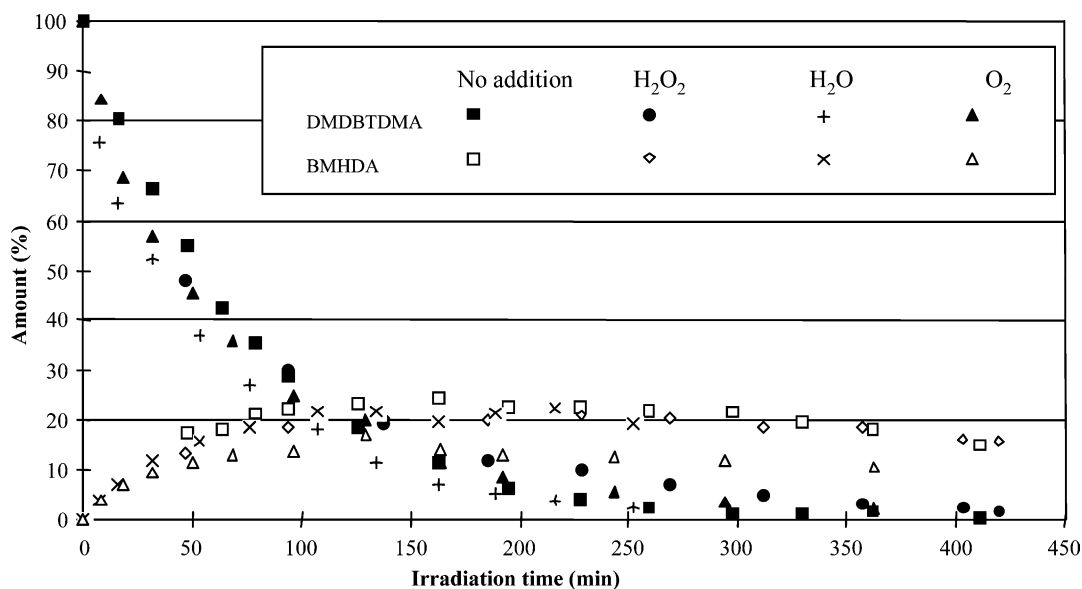


Fig. 6. Photo-oxidation of 0.5 mol l^{-1} DMDBTDMA solutions with oxidant addition or without.

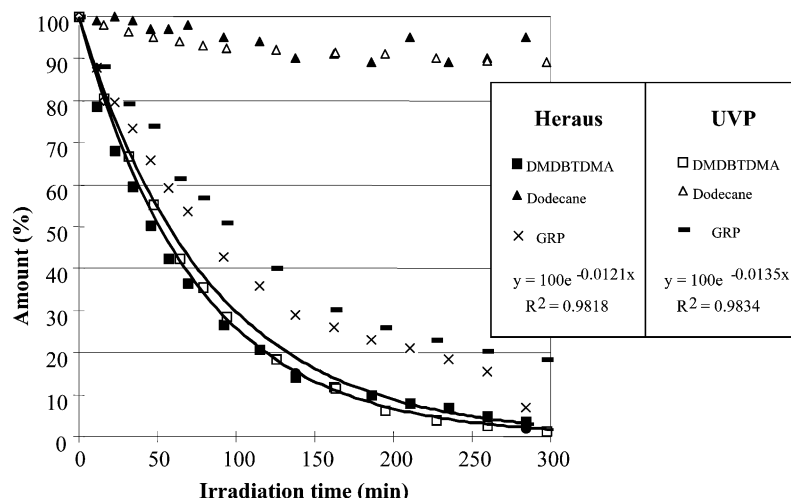


Fig. 7. Comparison of UVP and Heraus device efficiencies.

temperature difference due to lamp electric powers between both devices does not have an influence on the DMBTDMA degradation. This temperature does not increase a lot the evaporation of more volatile compounds because the lost volumes for an experiment are 0.2 and 0.4 ml for UVP and Heraus devices, respectively. The lost part is low (<3%) and can be considered as negligible. GRP values are close too even if the Heraus system seems a little more efficient. This fact can be explained by the observation of a more rapid degradation of BMHDA with Heraus lamp.

3.4.5. Influence of concentration

Experiments with four diluted solutions (Fig. 8) show that the same degradation can be obtained quickly when the solution is less concentrated. This fact confirms that a large amount of initial molecule cannot be destroyed due to limitant radiation from the lamp. Concentration ratios and kinetic constant ratios, that present close values, are reported in Table 4 for the four concentrations.

n-Dodecane is less sensitive to photo-oxidation than the diamide even if a more important degradation is observed when its concentration increase. This fact can

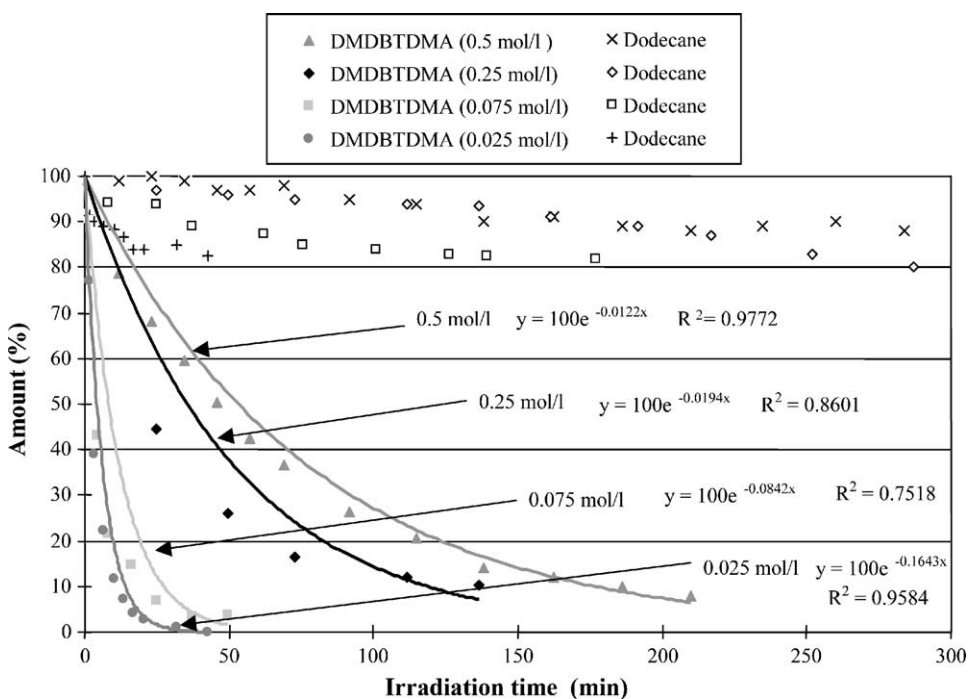


Fig. 8. Photo-oxidation of 0.5, 0.25, 0.075 and 0.0025 mol⁻¹ DMBTDMA solutions with Heraus device: evolution of DMBTDMA and dodecane.

Table 4
Comparison between concentration and kinetic constant ratios for DMDBTDMA degradation

Concentration (mol/l)	Kinetic constant (s ⁻¹)	Concentration ratio	Kinetic constant ratio
C ₁ = 0.5	K ₁ = 0.0122	C ₁ /C ₃ = 6.7	K ₃ /K ₁ = 6.9
C ₂ = 0.25	K ₂ = 0.0194	C ₁ /C ₂ = 2.0	K ₂ /K ₁ = 1.6
C ₃ = 0.0075	K ₃ = 0.0842	C ₂ /C ₃ = 3.3	K ₃ /K ₂ = 4.3
C ₄ = 0.0025	K ₄ = 0.1643	C ₃ /C ₄ = 3.0	K ₄ /K ₃ = 2.0

be correlated to the amount of irradiated molecule of solvent.

4. Conclusion

The photodegradation of tetra-alkyl malonamides has been carried out with low pressure mercury lamps (Heraeus 100 W and UVP 25 W). Both initial diamides present the same reactivity and the ether bond of DMDBDDEMA does not introduce an important weakness of the structure comparatively to DMDBTDMA. In order to destroy initial molecule solutions at 0.5 mol l⁻¹ in *n*-dodecane, the irradiation takes more than 300 min. Initial molecules lead to several photoproducts, which are mainly smaller malonamides, monoamides, formamides and carboxylic acids and that react to establish a degradation pathway. The presence of these by-products is taken into account in the global degradation with the calculation of the GRP that integrates the size and the amount of photo-products still present. The GRP shows that after 300 min irradiation time, around 20% of organic matter is not completely degraded due the presence of main photoproducts. The addition of some oxidants, such as hydrogen peroxide, molecular oxygen, or water does not have a significant influence on the photodegradation and both UVP and Heraeus lamps lead to similar destruction. The main factor is the diamide concentration, which allows quick destruction of initial molecule (30 min)

with diluted solution of DMDBTDMA at 0.025 mol l⁻¹ in *n*-dodecane. Photodegradation can be coupled to other destruction way (thermal oxidation, for example) in order to increase the degradation process.

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