Thermal and photo-oxidation of a potential extractant in nuclear fuel reprocessing

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Abstract

Malonamides have been investigated by the C.E.A. (Commissariat à l'Energie Atomique) to extract actinides (III) and lanthanides (III) from acidic nitrate nuclear waste solutions. The destruction of these potentially incinerable molecules has been tested in relatively soft conditions : thermal oxidation at temperatures below 250°C and photo-oxidation at short wavelengths (185-254 nm). Qualitative and quantitative analysis of main degradation products allows the comparison between these methods. Thermal oxidation leads to a rapid destruction of the initial molecule but numerous by-products and some black insoluble material appear, whereas photo-oxidation is slower but doesn't give so many by-products and any insoluble residues.

1 Introduction

C.E.A. has undertaken the development of the DIAMEX process, whose aim is the coextraction of actinides (III) and lanthanides (III) from high level liquid waste. Preliminary counter-current hot tests had confirmed the feasibility of the concept e.g. Madic & Hudson,[1].

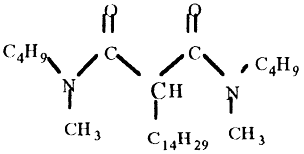
The extractants used are malonamides : $(\mathrm{RR'NCO})_2\mathrm{CHR''}$ with R, R', R'' alkyl radicals. The reference-extractant for this study is DBDMTDMA : *N,N'*-DiButyl, *N,N'*-DiMethyl, TetraDecyl MalonAmide. These molecules with only carbon, hydrogen, oxygen and nitrogen atoms are hence potentially incinerable.

This study deals with their destruction or at least, the minimisation of the final volume to be stored, thanks to relatively soft conditions : thermal oxidation at temperatures below 250°C and photo-oxidation at short wavelengths (185-254 nm).

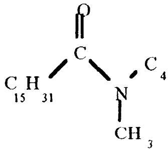
2 Materials and methods

2.1 Compounds

DBDMTDMA and its main degradation product BMHDA, (*N*-Butyl *N*-Methyl HexaDecanAmide), were provided by Panchim (France) with a purity of up to 99%. The developed formulae are :



DBDMTDMA



BMHDA

99% pure dodecane from Acros was used as a diluter and HPLC quality ethyl acetate from Rathburn as a solvent. The Internal Standard (I.S.) was hexadecane from Fluka with a GC purity of up to 98%.

2.2 Thermal oxidation device

1g of a 0,5 mol/L DBDMTDMA solution in dodecane is weighted in a 15 ml flask and then heated with an oil bath up to 250°C. A pure oxygen or an ozonated air flow can go through the whole solution. Ozonated air is produced by a Trailigaz laboratory ozonator. An adsorbent placed at the top of the condenser guarantees the recovery of volatile molecules. After thermal oxidation, 12 ml of ethyl acetate are added to the syrupy residues in the flask to collect them.

2.3 Photo-oxidation device e.g. Braun & al.,[2]

Experiments consist of the circulation of the 10 ml solution to be degraded in a 6.5 ml suprasil quartz spiral which surrounds the irradiation lamp.

Transactions on Ecology and the Environment vol 32, © 1998 WIT Press, www.witpress.com, ISSN 1743-3541

The UVP Pen-Ray lamp is a low pressure Hg, cold cathode with double bore suprasil quartz tubing. The main emission ray is at 254 nm but the 185 nm ray is also present. During irradiation, 50 µl are steadily pipeted from the solution, then diluted in 3 ml of ethyl acetate plus 50 µl of the I.S. solution.

2.4 Experimental methodology

Many factors influence thermal degradation. In order to quantify these influences and to find out the interactions between them, a methodological approach seemed to be required e.g. Sado & Sado,[3]. To represent the different Y responses, polynomial equations were postulated by using a 2^3 factorial design. Each model contained proportionality coefficients (a_i) according to the coded values (c_i) of the three factors as shown in eqn. (I).

$$Y = a_0 + \sum_{i=1}^{n} a_i c_i + \sum_{i=1}^{n}\sum_{j=1}^{n} a_{ij} c_i c_j + \sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n} a_{ijk} c_i c_j c_k \qquad \text{(I)}$$

The model was generated by the 3.0 NEMROD software, New Efficient Methodology for Research using Optimal Design e.g. Mathieu & Phan-Tan-Luu,[4].

The residual percentages of DBDMTDMA (Y_{C14}) eqn. (II) and dodecane (Y_{Dod}) eqn. (III) after thermal degradation, were studied.

$$Y_{C14} = \frac{n_{C14}^{exp}}{n_{C14}^{i}} * 100 \quad \text{with} \begin{cases} n_{C14}^{exp} : \text{residual DBDMTDMA} \quad (\text{mole}) \\ n_{C14}^{i} : \text{initial DBDMTDMA} \quad (\text{mole}) \end{cases} \qquad \text{(II)}$$

$$Y_{Dod} = \frac{n_{Dod}^{exp}}{n_{Dod}^{i}} * 100 \quad \text{with} \begin{cases} n_{Dod}^{exp} : \text{residual dodecane} \quad (\text{mole}) \\ n_{Dod}^{i} : \text{initial dodecane} \quad (\text{mole}) \end{cases} \qquad \text{(III)}$$

The mole number of BMHDA, the main degradation product of DBDMTDMA, was reported to the initial amount of DBDMTDMA to define a third response (Y_{BMHDA}) eqn. (IV).

$$Y_{BMHDA} = \frac{n_{BMHDA}^{exp}}{n_{C14}^{i}} * 100 \quad \begin{cases} n_{BMHDA}^{exp} : \text{amount of BMHDA} \quad (\text{mole}) \\ n_{C14}^{i} : \text{initial DBDMTDMA} \quad (\text{mole}) \end{cases} \qquad \text{(IV)}$$

2.5 Analysis systems

All the analysis are based on Gas Chromatography (G.C.) using three different detections: a Flame Ionisation Detection (F.I.D.) for quantitative analysis, a Fourier Transform InfraRed detection (F.T.I.R.), and a Mass Spectrometer detection (M.S.) for qualitative analysis.

3 Results

3.1 Qualitative analysis :

The major degradation products identified after thermal oxidation or photo-oxidation (figure 1) are almost the same. The main difference between the two methods of destruction is not the nature but the relative quantity of the formed products.

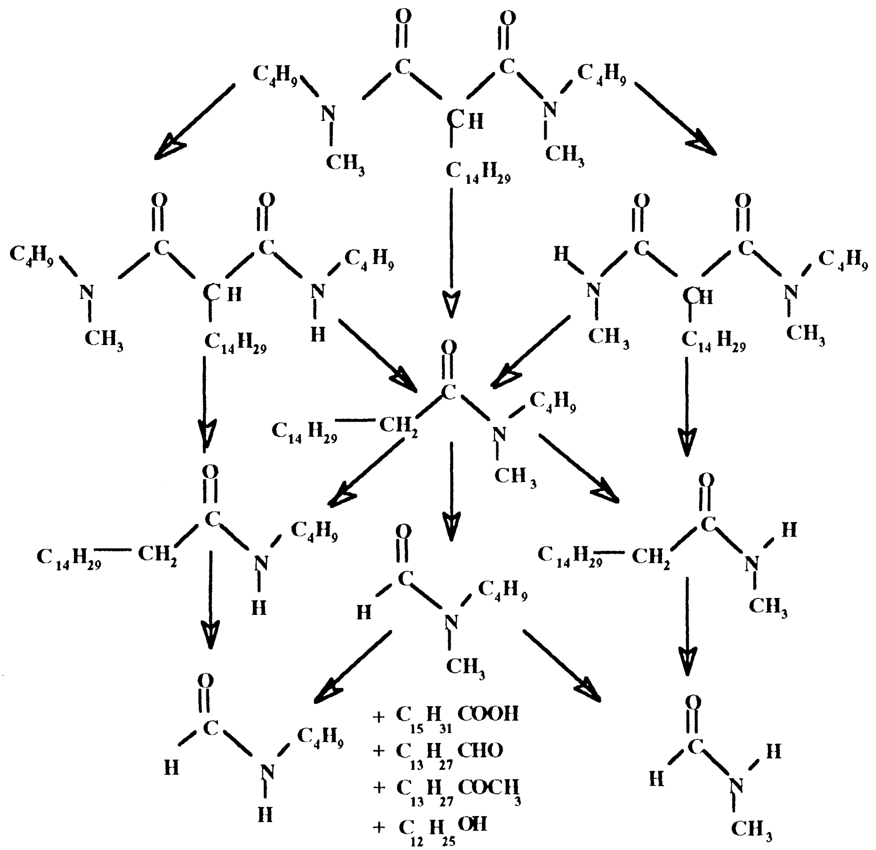


Figure 1 : Proposition of a degradation pathway for DBDMTDMA thermal or photo-oxidation.

3.2 Quantitative analysis

3.2.1 Results of the thermal oxidation experimental design

3.2.1.1 Constant parameters These conditions have been retained after preliminary experiments. The open batch reactor has been prefered to the closed Wheaton tube which fast leads to a lack of oxygen e.g. Dagnac & al.,[5]. 250°C has been chosen in the range of moderate temperatures 150°C-250°C because of its important effect.

The gaseous flow rate was fixed between 2 and 4 ml/min to prevent the loss of the most volatil by-products. The initial mass of product which can be considered as significant is 1 g of a 0.5 mol/L DBDMTDMA solution in dodecane. This molecule is used to simulate the industrial diluent.

3.2.1.2 Variable parameters Table 1 indicates the variation of the parameters whose influence and interactions were studied in this experimental design.

c_i level	Variable parameters		
	Time (hour)	Humidity	Atmosphere
- 1	1	No	Pure oxygen
0	1.5	-	-
+ 1	2	50 mg of water (5% w/w)	55 mg/L of ozon in air

Table 1 : parameters variation for the experimental design.

The time is a continuous factor, thus this factor has been evaluated on an intermediate level coded 0 and corresponding to 1h30 of degradation. The two other factors are qualitative ones : between the two limit values, the intermediate level has no sense for the experimental design. The addition of 50 mg of water totally ensures the saturation of the 1g solution because 2.3 mg of water saturate 1 g of a 0.5 mol/L DBDMTDMA solution e.g. Nigond,[6].

3.2.1.3 Experimental results The first eight tests of table 2 were strictly necessary for modelling but the last four ones allow a more valid model.

	Time	Humidity	Atmosphere	Y_{C14}	Y_{BMHDA}	Y_{Dod}
1	1 hour	No	Oxygen	38,3	3,6	71,0
2	2 hours	No	Oxygen	20,2	6,2	61,5
3	1 hour	50 mg water	Oxygen	24,5	6,5	64,2

4	2 hours	50 mg water	Oxygen	13,1 - 11,2	10,4 - 11	67,7 - 66,2
5	1 hour	No	Ozonated air	53,7	2,1	69,7
6	2 hours	No	Ozonated air	46,5	3,9	72,3
7	1 hour	50 mg water	Ozonated air	45,4	4,8	70,9
8	2 hours	50 mg water	Ozonated air	26,9	10,3	66,7
9	1 hour 30	No	Oxygen	27,6	7,1	66,2
10	1 hour 30	No	Ozonated air	48,9	3,3	62,2
11	1 hour 30	50 mg water	Oxygen	16,3	7,2	65,0
12	1 hour 30	50 mg water	Ozonated air	38,1	5,5	75,6

Table 2 : conditions and results for thermal oxidation of 1g of 0.5 mol/L DBDMTDMA solutions at 250°C, 2-4 ml/min O_2 gas flow rate.

3.2.1.4 Models The different coefficients A_i and B_i of the linear combinations for DBDMTDMA and BMHDA responses are defined in Eqns (V) and (VI)

$$\mathbf{Y_{C14}} = A_0 + A_1*(\mathit{Time}) + A_2*(\mathit{Humidity}) + A_3*(\mathit{Atmosphere}) + A_{12}*(\mathit{Time}*\mathit{Humidity}) + A_{13}*(\mathit{Time}*\mathit{Atmosphere}) + A_{23}*(\mathit{Humidity}*\mathit{Atmosphere}) + A_{123}*(\mathit{Time}*\mathit{Humidity}*\mathit{Atmosphere}) \quad \text{(V)}$$

$$\mathbf{Y_{BMHDA}} = B_0 + B_1*(\mathit{Time}) + B_2*(\mathit{Humidity}) + B_3*(\mathit{Atmosphere}) + B_{12}*(\mathit{Time}*\mathit{Humidity}) + B_{13}*(\mathit{Time}*\mathit{Atmosphere}) + B_{23}*(\mathit{Humidity}*\mathit{Atmosphere}) + B_{123}*(\mathit{Time}*\mathit{Humidity}*\mathit{Atmosphere}) \quad \text{(VI)}$$

Table 3 gives the coefficients of each variable factor and the interactions between these parameters. Coefficients whose significant probabilities (Signif. %) are greater than 95 % are presented in bold.

	Constant	Time	Humidity	Atmos phere	Interactions			
Y_{C14}	A_0	A_1	A_2	A_3	A_{12}	A_{13}	A_{23}	A_{123}
Coefficients	**33.24**	**-6.97**	**- 5.96**	**10.01**	-0.65	0.55	-0.49	**-2.18**
Signif. %	>99.9	>99.9	>99.9	>99.9	76.1	69.9	72.7	>99
Y_{BMHDA}	B_0	B_1	B_2	B_3	B12	B13	B23	B123
Coefficients	**5.95**	**1.79**	**1.59**	**- 0.97**	0.69	0.03	0.30	0.23
Signif. %	>99.9	> 99	> 99	>95	84	5.7	55.9	38.8

Table 3 : Model coefficients for responses Y_{C14} and Y_{BMHDA}

Y_{C14} : Residual DBDMTDMA model The atmospheric parameter is the most influential factor, prior to time and finally humidity.

Coefficients linked to interactions except A_{123} are weak and not significant, surprisingly for ozonated air and water. Indeed, the ozone-water mix leads theoretically to very reactive hydroxyl radicals.

To explain the observed behaviour, some hypothesis can be proposed :

- hydroxyl radicals may not be formed because :
  - the ozone concentration or the water volume are too weak;
  - water or ozone act first on the initial molecule or on the by-products

- hydroxyl radicals are formed but they rather act on by-products of degradation than on DBDMTDMA.

It appears on one hand that ozonated air is less effective than pure oxygen on DBDMTDMA degradation, and on the other hand that water increases the degradation rate.

Y_{BMHDA} : BMHDA model Only coefficients related to the interactions are less significant than 95%. Most important factors are therefore time, followed by humidity, then atmosphere, time-humidity interaction and finally the two other interactions. Since BMHDA can be observed so clearly, BMHDA is more resistant to thermal oxidation than DBDMTDMA. Moreover, the fact that one more hour of degradation increases the BMHDA percentage shows that the BMHDA formation-degradation balance is still in favour of the appearance of this product after one hour.

Y_{Dod} : Residual dodecane model No studied factors appeared influential. The average 30% of dodecane degradation are therefore due to the values of constant parameters.

3.2.1.5 Deviation between experimental and calculated values To evaluate the quality of the model responses, variation (% VAR.) between experimental result and predicted value is determined according to eqn. (VII) and presented in table 4.

$$\%\,\text{VAR.} = \frac{|\text{Exp.} - \text{predict.}|}{\text{Exp.}} \times 100 \qquad \text{(VII)}$$

	Y_{C14}			Y_{BMHDA}		
	Exp.	Predict	VAR.	Exp.	Predict.	VAR.
1	38.3	37.8	1.3	3.6	4.3	19.4
2	20.2	19.7	2.5	6.2	6.9	11.3
3	24.5	23.8	2.9	6.5	6.0	7.7
4	13.1-11.2	11,8	9.9-5,4	10.4-11.0	10.4	0-5.4
5	53.7	53.3	0.7	2.1	2.2	4.8
6	46.5	46.1	0.9	3.9	4.0	2.6
7	45.4	46.1	1.5	4.8	4.1	14.6
8	26.9	27.6	2.6	10.3	9.6	6.8
9	27.6	28.7	4	7.1	5.6	21.1
10	48.9	49.7	1.6	3.3	3.1	6.1
11	16.3	17.8	9.2	7.2	8.2	13.9
12	38.1	36.8	3.4	5.5	6.9	25.4

Table 4 : Deviation between experimental and predicted values of the DBDMTDMA thermal oxidation experimental design

For DBDMTDMA, except for experiments 4,11, relative differences between experimental values and calculated values remain lower than 5 %, value close to the experimental error. The model can be therefore considered as acceptable. For BMHDA, these differences are clearly superior. This model is less accurate than for DBDMTDMA, but still significant.

3.2.1.6 Conclusion about thermal-oxidation In the range studied, optimum destruction conditions are 2 hours with a pure oxygen atmosphere and presence of water. The result is about 90% destruction of DBDMTDMA after 2 hours with 11% residual BMHDA.

3.2.2 Results of photo-oxidation

3.2.2.1 Introduction The phenomenon used is photon absorption by studied molecules in the area of the UltraViolet (UV) range. The absorption range for both amides is between 200 and 250 nm.

3.2.2.2 Photo-oxidation of DBDMTDMA and BMHDA solutions
Since BMHDA was the main degradation product of DBDMTDMA, we separately tested the photo-oxydation of both molecules in the same experimental conditions.

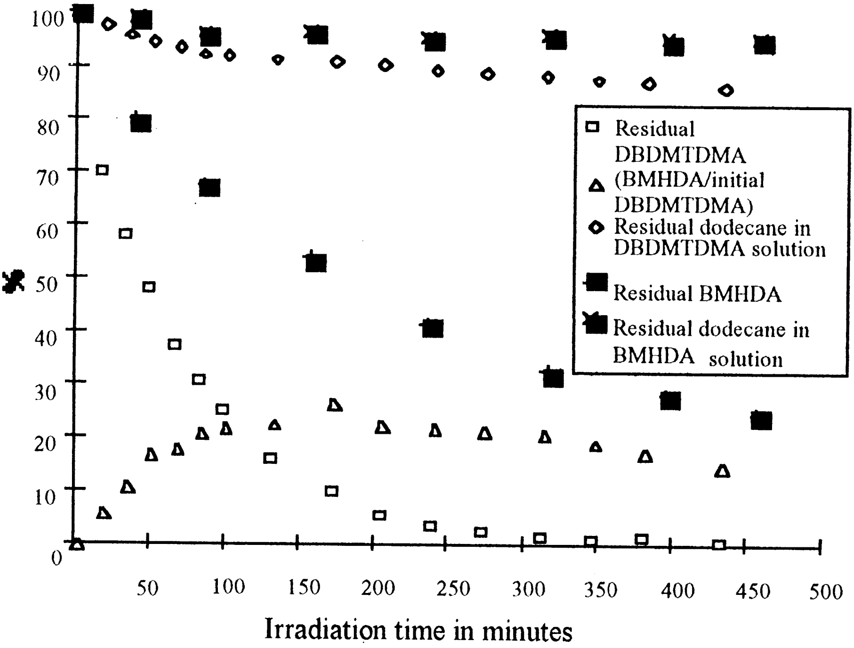


Figure 2 : Photo-oxydation kinetics of DBDMTDMA and BMHDA 0.5 mol/L solutions in dodecane, at room temperature, under ambient air.

DBDMTDMA is degraded with a faster kinetic than the BMHDA (figure 2). BMHDA is therefore more resistant to the photo-oxidation than the initial diamide.

3.2.2.3 Conclusions on photo-oxydation This destruction method seems adequate but a bit slow : 90% of initial DBDMTDMA and only 50% of initial BMHDA are degraded after 3 hours of irradiation. Thus, the focus for further experiments will be on photo-oxydation of more diluted solutions and their saturation with hydrogen peroxyde solution or oxygen. A new Hg low pressure doped lamp with a greater emission at 185 nm will also be tested.

4 Conclusion

Thermal oxidation at 250°C under a pure oxygen flow, leads to a rapid destruction of the initial compound but numerous by-products and some black insoluble material appear.

Due to the weak power of the lamp used, photo-oxidation requires more time to achieve the same DBDMTDMA degradation yield but leads to less numerous by-products and no insoluble residues. For both methods, BMHDA is the main degradation product and shows a greater stability than the initial DBDMTDMA. Dodecane is more resistant to photo-oxydation than to thermal oxidation in the studied conditions. An index of destruction based on the molecular weight of all residual products will be calculated so as to compare more globally the efficiencies of thermo-oxidation and photo-oxidation. Thermal oxidation after photo-oxidation will also be studied.

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