Hydrolysis of Nitramines

Final Report October 2011

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Table of Contents

Executive Summary 1

1 Objectives and scope of work 3
1.1 Scope of work 3

2 HSE 3

3 Experimental 3
3.1 Chemicals 3
3.2 Instruments and procedure 4

4 Results 4
4.1 Effect of salt 8

5 Literature 9

Executive Summary

The hydrolysis of dimethylnitramine, $(CH_3)_2NNO_2$, and 2-(nitroamino)-ethanol, $HOCH_2CH_2NHNO_2$, has been studied at pH= 5, 7 and 9 over a period of more than 40 days. The lifetime of the two nitramines with respect to hydrolysis is more than 1 year and is independent on pH in the region 5-9. The effect of salt was studied in 2.5 wt% NaCl solutions at pH = 5; no significant decrease in hydrolysis lifetime was observed.

It is concluded that primary and secondary nitramines do not undergo hydrolysis to any significant degree under relevant environmental conditions.

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Hydrolysis of nitramines

1 Objectives and scope of work

The objective is to determine the environmental fate of nitramines in the aqueous compartment.

1.1 Scope of work

The hydrolysis of dimethylnitramine and MEA-nitramine will be studied in acidic, neutral and basic water during a 4-week period under abiotic conditions.

2 HSE

The project involved handling of hazardous chemicals and was carried out as required by statutes and regulations.

The Standard Operational Procedure (SOP) in the UiO laboratory is that all compounds under study, including possible degradation products, are treated as potentially carcinogenic unless other information is available. It is noted that:

- Solutions were prepared in a fumehood (protective glowes)
- Samples were transferred to cuvettes in a fumehood.
- Cuvettes were sealed (airtight).
- Glassware cleaned with 5M H_2SO_4.
- Cuvettes washed in 5M H_2SO_4 after use.
- All solutions acidified with 5M H_2SO_4 and left for 2 days before being deposited for normal destruction.

The University of Oslo is a Governmental institution that follows HSE rules and regulations according to Norwegian Law. UiO is not required to produce HSE data sheets for compounds synthesized for research purpose. The HSE-manual can be found here:

http://www.kjemi.uio.no/intern/organisasjonsutvikling/hms/hse-manual/

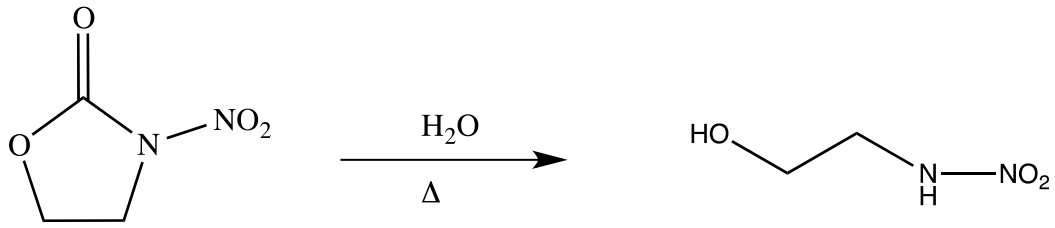
No accidents or near accidents have occurred during the project lifetime.

3 Experimental

3.1 Chemicals

The sample of dimethylnitramine was used as received from Prof. Yngve Stenstrøm, UMB. 16 mg dimethylnitramine was dissolved in ca. 1 L Type-II water and left overnight under dark conditions ($\approx 2\times10^{-4}$ M). No attempt was made to prepare a quantified solution, the main issue was to have a peak absorbance around 1.

The MEA-nitramine, 2-(nitroamino)-ethanol, was synthesized by hydrolysis of 3-nitro-oxazolidin-2-one:



50 mg 3-nitrooxazolidin-2-one was dissolved in ca. 2 mL water. The solution was heated overnight at 45-50 °C. Around 1/3 of the solution was added to ca. 1 L Type-II water and left overnight under dark conditions. No attempt was made to prepare a quantified solution, the main issue was to have a peak absorbance around 1 ($\approx 2\times10^{-4}$ M).

Three 250 mL solutions were prepared for each nitramine, and pH adjusted to respectively 5.0±0.2, 7±0.2 and 9±0.2 by adding dilute solutions of NaOH respectively HCl.

3.2 Instruments and procedure

New, airtight QS cuvettes were irradiated for 20 min. by germicide UV radiation (λ = 254 nm). 18 samples were prepared: (2 nitramines) × (3 parallels) × (3 different pH). Each cuvette was rinsed by a solution 2-3 times and sealed by the screwcap. No attempts were made to ensure exactly identical solutions in the cuvettes.

UV spectra were recorded employing an Agilent 8453E photodiode array spectrophotometer. The spectra were recorded in the wavelength range from 190 to 1100 nm with sampling intervals of 1 nm and with an integration time of 0.5 s. The photometric accuracy is <±0.005 A at 1A (NIST 930e). Spectra (reference and samples) were recorded once a day, Monday through Friday, in the period from August 3 to September 16.

4 Results

Nitramines absorb in the UV around 230 nm, see e.g. McQuaid *et al.*[1] Figure 4.1 shows the UV-VIS spectra of ca. 0.17 mM dimethylnitramine solutions at pH 5, 7 and 9. It can be seen that there is a small diference in the spectra below 200 nm. This is believed to be due to chlorine ions.

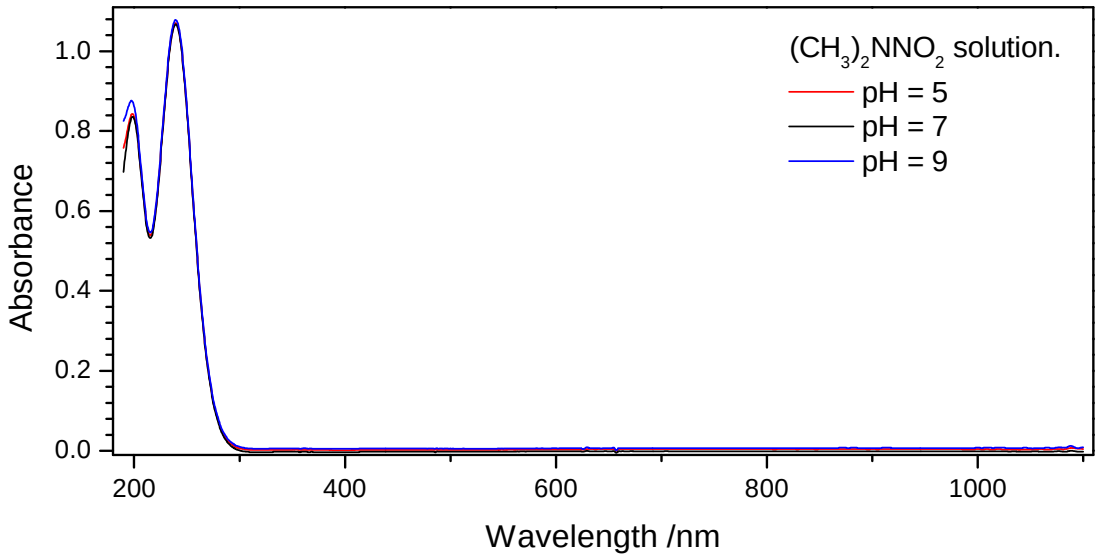


Figure 4.1. UV-VIS spectra (190–1100 nm) of dimthylnitramine solutions at pH = 5, 7 and 9.

A semi-automatic methodology was defined to reduce human bias in the quantitative analysis of the spectra: (1) the spectra were converted from wavelength to wavenumber units preserving the absorbance values, (2) the spectra were fitted by 2 Lorenzian/Gaussian bands, Figure 4.2, and the area of the 240 nm band (41800 cm^{-1}), IB_{240}, is taken as a measure of the nitramine concentration in the solution.

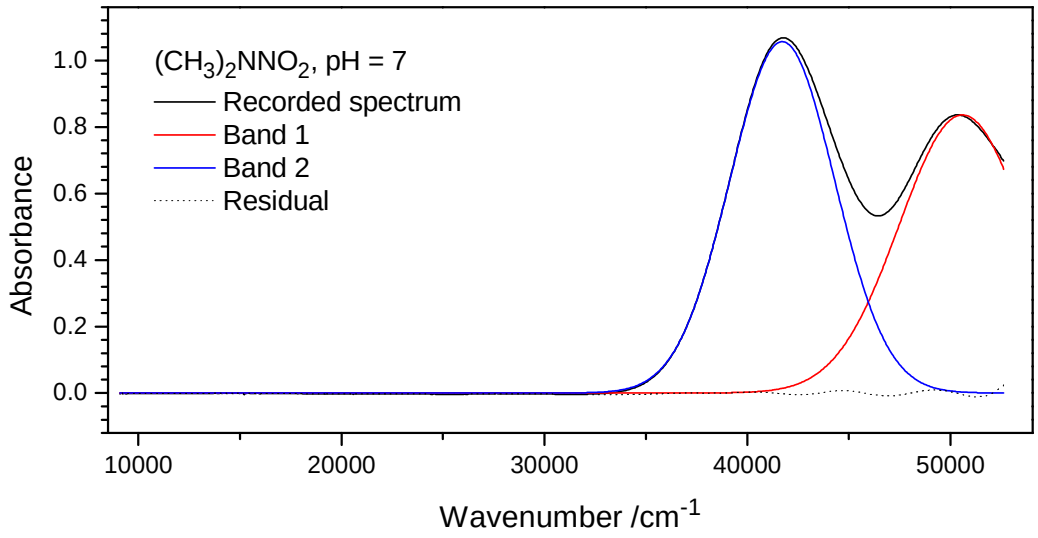


Figure 4.2. Example of spectral fitting. The UV-spectrum of aqueous dimethylnitramine at pH=7 can be accurately fitted by 2 Gaussian-shaped bands. The residual rms error of fit is around 0.005 A.

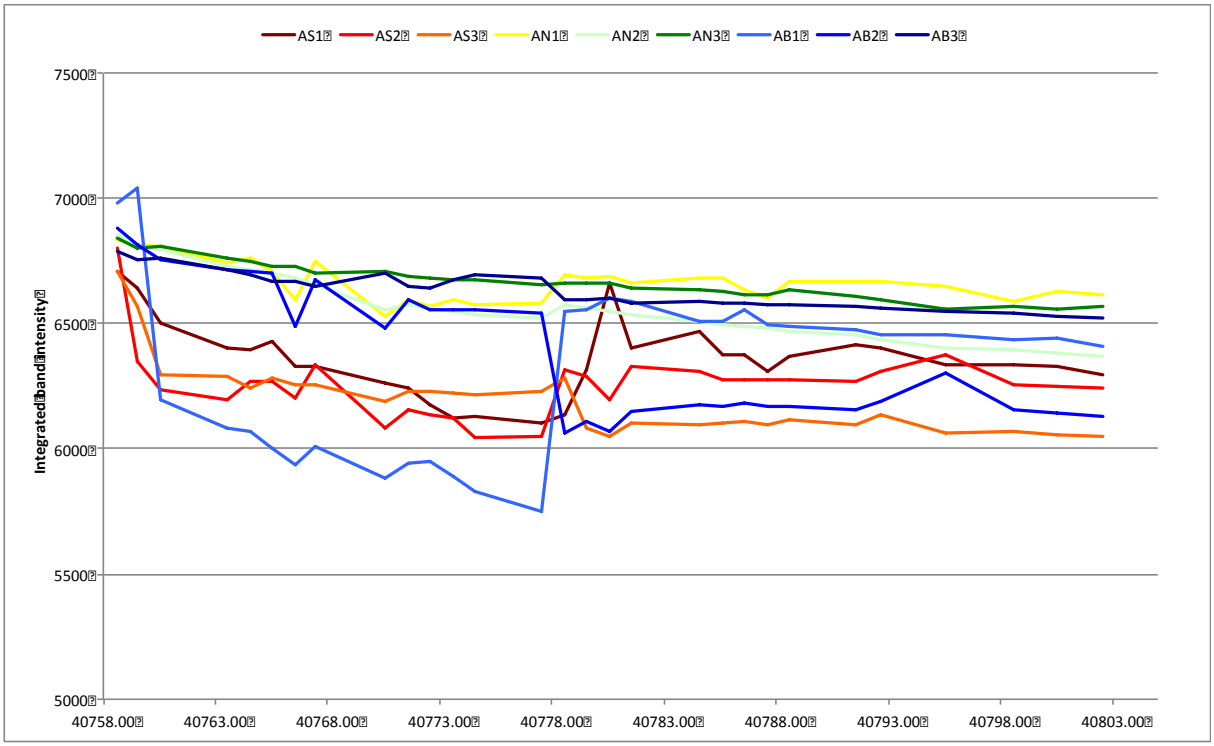


Figure 4.3. Integrated band intensity, IB_{240}, of the 240 nm band of aqueous dimethylnitramine as a function of time. Results from nine different samples are included. Sample code: A, dimethylnitramine; S, pH=5; N, pH=7; B, pH=9; 1-3, sample no.

It can be seen from Figure 4.3 that there is slow decrease inn the integrated band intensity with time. There is no similar trend in the peak wavenumber, in the band width or in the band shape. There is no significant difference between the acidic, neutral and basic samples.

The nitrate ion presents two UV absorption bands in water: a broad and very intense band at 220 nm with a shoulder around 240 nm, and a less intense band at 300 nm (first reported by Massol 1914[2]). Dimethylamine also show absorption in the region around 240 nm in the gas phase. However, in the aqueous phase this band is blue shifted and is orders of magnitude weaker than the nitramine band. This decrease in intensity of the 240 nm band is therefore interpreted in terms of hydrolysis: $(CH_3)_2NNO_2 + H_2O \rightarrow (CH_3)_2NH_2^+ + NO_3^-$. Assuming the hydrolysis to be 1 first-order process, the integrated band intensity can then be described by:

$$IB_{240}(t) = IB_{240}(0) \times \exp(-k_{hydrolysis} \times t)$$

Figure 4.4 summarises the data plotted in the form $\ln(IB_{240}(t)/IB_{240}(t=0))$.

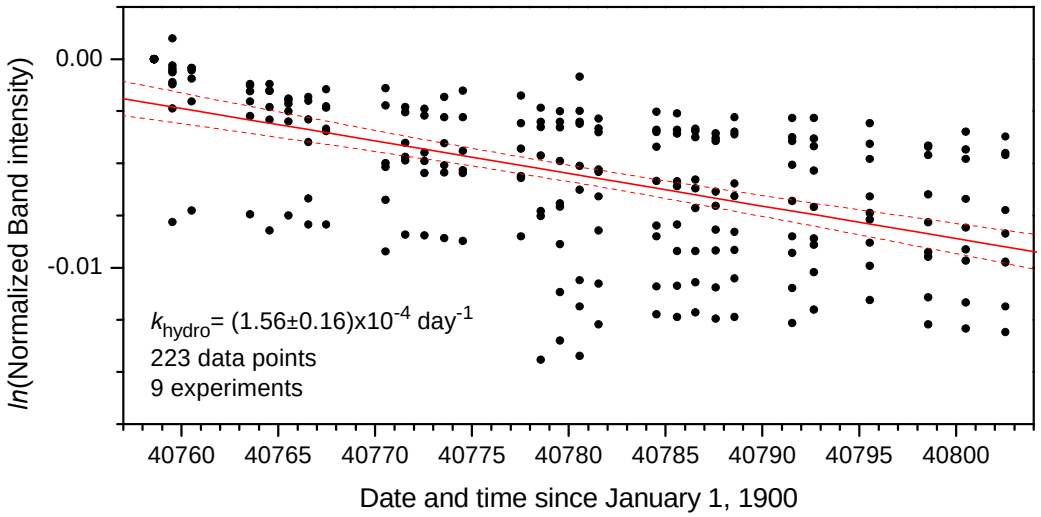


Figure 4.4. Least-squares fit of dimethylnitramine relative concentration data as a function of time. The dotted curves span the 95% confidence limit of the decay line.

The data suggest that the lifetime of DMNA with respect to hydrolysis is independent upon pH in the region 5-9, and that $k_{hydrolysis}$ is $(1.56 \pm 0.16) \times 10^{-4}$ day^{-1}. This corresponds to a hydrolysis lifetime of 18 ± 2 year. Taking instrumental stability and photometric accuracy, and the additional uncertainty introduced in the spectrum analysis (curve fitting) into consideration it is concluded that the hydrolysis lifetime of dimethylnitramine is more than 1 year.

It was mentioned above that aqueous solutions of amines and the nitrate ion have absorption bands in the region around the nitriamine bands. Figure 4.5 compares the spectra of the MEA nitriamine (pH = 5) obtained on day 1 and 88 days later with spectra of aqueous solutions of MEA and KNO_3 (both $\approx 10^{-3}$ M). It can be seen that (a) the MEA nitramine spectrum has decreased in intensity during 88 days (although the decrease is partly due to a reduction of the stray-light background below 200 nm), and (b) the band shape of the NO_3^- shoulder at 240 nm differs from that of the nitramine band such that a systematic error in the integrated band intensity of the nitramine can be ruled out (there is no significant change in the nitramine band shape during the experiment).

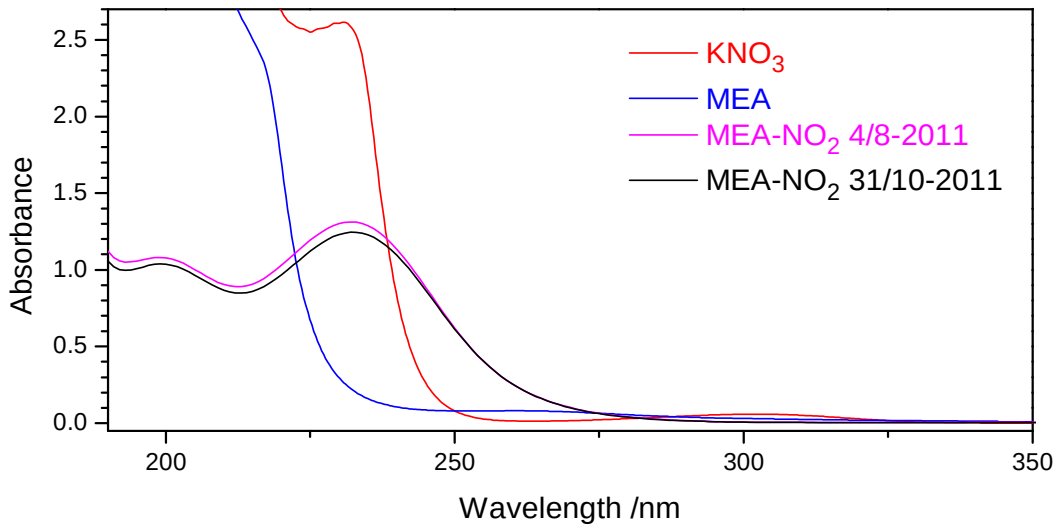


Figure 4.5. UV spectra of aqueous solutions of KNO_3, MEA, and of a MEA-nitramine sample in a sealed cuvette obtained on August 4 and October 31, 2011.

The MEA-nitramine spectra were analysed as described above for DMNA. Figure 4.6 shows the obtained integrated band intensities, IB_{240}, as a function of time. It can be seen that there is a very slow decrease in the integrated band intensities. There is no similar trend in the peak wavenumber, in the band width or in the band shape. There is no significant difference between the acidic, neutral and basic samples. Figure 4.7 summarises the data plotted in the form $\ln(IB_{240}(t)/IB_{240}(t=0))$.

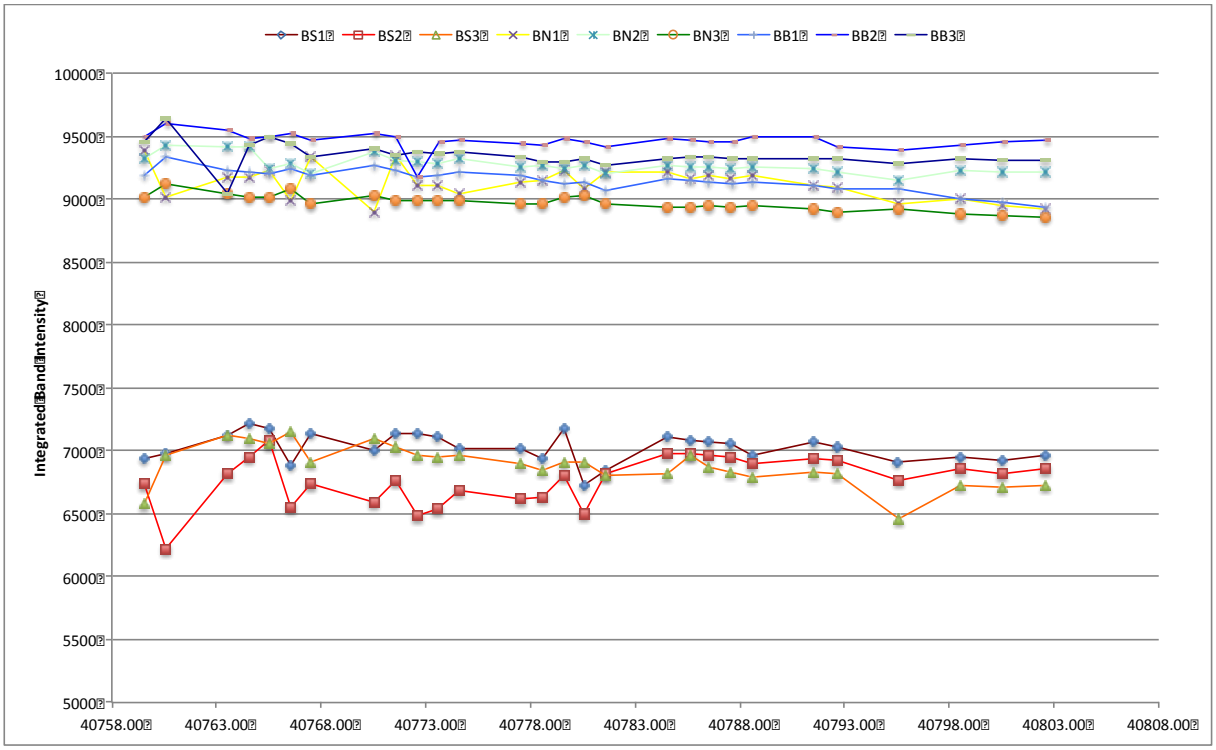


Figure 4.6. Integrated band intensity, IB_{240}, of the 240 nm band of aqueous MEA-nitramine as a function of time. Results from nine different samples are included. Sample code: B, MEA-nitramine; S, pH=5; N, pH=7; B, pH=9; 1-3, sample no.

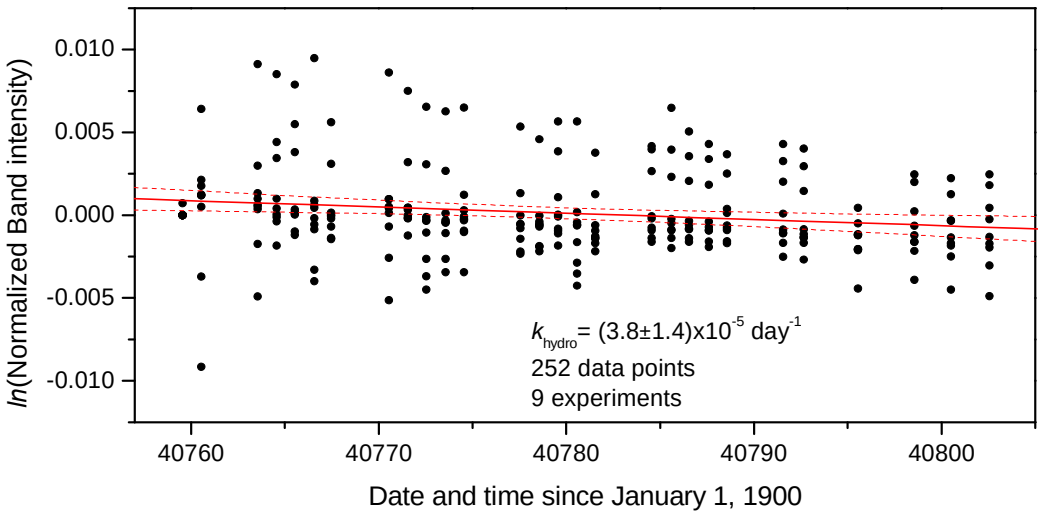


Figure 4.7. Least-squares fit of MEA-nitramine relative concentration data as a function of time. The

The data suggest that the lifetime of MEA-nitramine with respect to hydrolysis is independent upon pH in the region 5-9, and that $k_{\text{hydrolysis}}$ is $(3.8 \pm 1.4) \times 10^{-5}$ day^{-1}. This corresponds to a hydrolysis lifetime of 72 ± 26 year. Taking instrumental stability and photometric accuracy, and the additional uncertainty introduced in the spectrum analysis (curve fitting) into consideration it is concluded that the hydrolysis lifetime of MEA-nitramine is more than 1 year.

4.1 Effect of salt

The effect of salt on the hydrolysis rate was investigated by adding 2.5 g NaCl to 100 mL solutions of dimethylnitramine and MEA-nitramine with pH = 5. Spectra of the two solutions were recorded with 17 days interval. Figure 4.8 shows the spectra obtained of the DMNA solution, while Figure 4.9 shows the spectra obtained for the MEA-nitramine solution.

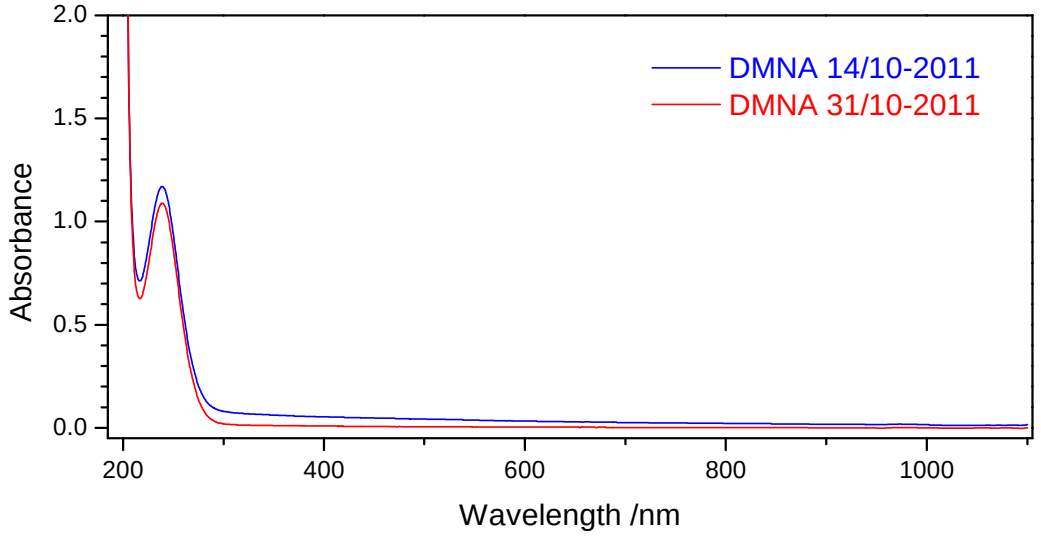


Figure 4.8. UV spectra of DMNA in a 2.5 wt% NaCl aqueous solution obtained at October 14 and 31, 2011.

The two spectra of DMNA differ in a sloping baseline, but are otherwise identical within 1%. From this one may extract a hydrolysis lifetime of >4 year.

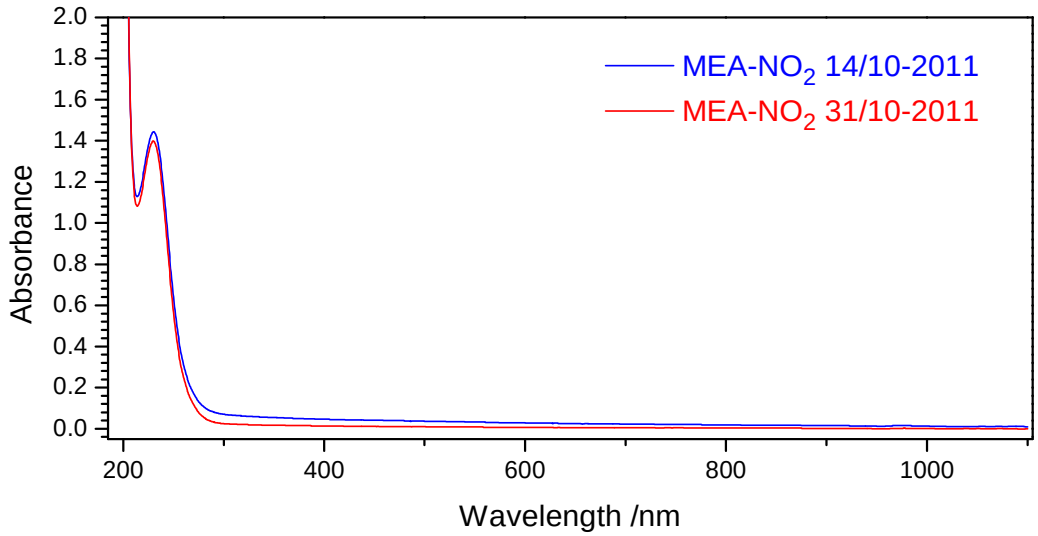


Figure 4.9. UV spectra of MEA-nitramine in a 2.5 wt% NaCl aqueous solution obtained at October 14 and 31, 2011.

The two spectra of MEA-nitramine differ in a sloping baseline, but are otherwise identical within 1%. From this one may extract a hydrolysis lifetime of >4 year.

It can be concluded that the lifetime of the two nitramines, DMNA and MEA-nitramine, with respect to hydrolysis in salt-water is more than 1 year.

5 Literature

(1) McQuaid, M. J.; Sausa, R. C. *Appl. Spectrosc.* **1991**, *45*, 916.
(2) Massol; Faucon *Compt. rend.* **1914**, *159*, 174.