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Development of a new on-line mass spectrometer to study the reactivity of soluble organic compounds in the aqueous phase under tropospheric conditions: Application to OH-oxidation of *N*-methylpyrrolidone

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Abstract

A new on-line analyser was developed to study OH-oxidation of soluble organic compounds in the aqueous phase. The system consisted in the coupling of an aqueous phase photo-reactor with a triple quadrupole mass spectrometer equipped with an electrospray ionisation source (ESI). The system was operated in both positive (ESI-MS$^+$) and negative (ESI-MS$^-$) modes, and in (ESI-MS–MS$^+$) mode for several parent ions. The system was validated by comparison with results obtained by HPLC-UV, during the OH-oxidation of *N*-methylpyrrolidone (NMP) in the aqueous phase. The rate constant of the reaction was determined at four temperatures ($\ln(k_{\mathrm{OH}}) = (24.4 \pm 1.1) - (760 \pm 320)/T$), showing that NMP is highly reactive in the aqueous phase, thus its reaction products should significantly influence the water droplet's composition. The results of the reaction products' study proved that the on-line analyser was highly promising, as it allowed us to detect the formation of 66 different ions, among which 24 correspond to identify reaction products. The main reaction products identified were succinimide, *N*-methylsuccinimide, formyl-pyrrolidone, *N*-hydroxymethylpyrrolidone, 5-hydroxy-*N*-methylpyrrolidone, 2-pyrrolidone, methylamine, formamide, acetamide, *N*-methylformamide, *N*-ethylacetamide and dimethylacetamide. The time profiles of these compounds are presented and a chemical mechanism is suggested for the reaction of OH radicals with NMP in the aqueous phase. The new on-line system also detected the formation of high molecular compounds (compared to the parent compound NMP), up to 300 amu, with mass intervals ranging from 13 to 18 amu. The processes leading to such compounds are discussed.

Keywords: Aqueous phase photo-reactor; On-line mass spectrometry; *N*-Methylpyrrolidone; Kinetic rate constants; OH-oxidation; Reaction products; Chemical mechanisms; High molecular reaction products

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1. Introduction

Atmospheric droplets of clouds and fogs play an important role in atmospheric chemistry. Their chemical composition is influenced by the composition of the cloud condensation nuclei (CCN) and by the surrounding gas phase. Chemical and photochemical reactions occur in the droplets, thus influencing their chemical composition. Key species of this chemistry are free radicals (e.g., OH, HO_2/O_2^-, NO_3, Cl, Cl_2^-, SO_4^-, etc.) produced by photoreactions which can react with dissolved organic matter. Among these radicals, one of the most efficient oxidizing species is the OH radical [1,2]. Many studies have dealt with aqueous phase reactivity, focusing on the kinetic aspect [3,4]. In comparison, very few authors have studied the reaction products and the mechanisms occurring in water droplets under atmospheric conditions [5–10]. This lack is due to the complexity of such experiments: the time profiles of the reaction products' concentrations, needed to understand the mechanisms involve the simultaneous use of different analytical methods. This imposes to store and/or prepare samples before their analysis. As a consequence, the number of reaction products increases with the parent molecular size, thus increasing the analytical needs and the problems of identification.

This study presents a new on-line technique suitable to identify a large number of reaction products. This technique consists in the coupling of an aqueous phase simulation chamber with a mass spectrometer. After the description of this technique,

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we present the first tests performed on the OH-oxidation of *N*-methylpyrrolidone (NMP). This compound is currently used in the industry as a substitute of chlorinated solvents and also in various industrial processes such as synthesis and formulation of pesticides, cosmetics, pigments, drugs, etc. NMP is also used as a cleaning agent of microelectronics [11,12]. Previous gas phase studies have shown that NMP reacts quickly with OH and NO_3 radicals and its direct photolysis and ozonolysis are very slow [13]. Its atmospheric gas phase lifetime (towards OH radicals) is moderate (13 h, for $[OH] = 10^6$ molec cm^{-3} [14]), and it is a highly soluble compound ($K_H = 6.4 \times 10^4$ M atm^{-1} [15]), thus NMP is likely to enter into tropospheric droplets. Nevertheless, due to its recent use in the industry, no available data exist at the moment for its atmospheric metrology in the gas and the aqueous phases. *N*-Methylpyrrolidone is a medium size molecule (MW = 99 g mol^{-1}), containing five carbon atoms, so its OH-oxidation may give rise to a large number of products. The present work was aimed at determining, under tropospheric conditions, the OH-oxidation rate constant of NMP and the reaction products formed in the aqueous phase. Two different types of experiments were conducted to determine, respectively (i) the kinetics and (ii) the reaction products formed, and the time profiles of their concentrations.

2. Chemical reagents

The following chemicals were used in this study without further purification: H_2O_2 (not stabilized, Fluka, 30% weight), $FeSO_4$ (Prolabo), *N*-methylpyrolidone (NMP) (Sigma–Aldrich, more than 99%), methyl-ethyl-ketone (MEK) (Fluka, more than 99.5%), methyl-*iso*-butyl ketone (MIBK) (Fluka, more than 99%), succinimide (Sigma–Aldrich, 98%), methylamine (Sigma–Aldrich, 40%), *N*-ethylacetamide (Sigma–Aldrich, 99%), *N*-methylsuccinimide (NMS) (Sigma–Aldrich, 99%), *N*-hydroxy-methylpyrrolidone (NHMP) (Sigma–Aldrich), acetamide (Sigma–Aldrich, 98%), formamide (Sigma–Aldrich, 98%), *N*-methylformamide (NMF) (Sigma–Aldrich, 99%), 2-pyrrolidone (2P) (Sigma–Aldrich, 99%) and dimethylacetamide (Sigma–Aldrich, 99%). Aqueous solutions were prepared using purified water from a Millipore MilliQ system including reverse osmosis, micro-filtration, nuclear-grade deionization and activated carbon modules (the resistivity of the purified water was greater the $1.8 \times 10^7\ \Omega\ cm^{-1}$). Organic solvents used for HPLC analysis were at HPLC grade (Acros organics).

3. Kinetic studies of OH-oxidation of NMP

The Fenton reaction (r1) was used to generate OH radicals in the aqueous phase at pH 2 and in the dark (for details see reference [16]):

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + OH \qquad (r1)$$

The OH-oxidation rate constants were determined using the relative kinetic method. Methyl-ethyl-ketone (MEK) and methyl-*iso*-butylketone (MIBK) were used as reference compounds with the following expressions to determine the Arrhenius parameters of NMP (more details about reference compound values can be found in reference [16]):

$$\ln k_{MEK}(T) = (26.2 \pm 1.0) - \frac{(1600 \pm 300)}{T} \quad [16] \qquad (1)$$

$$\ln k_{MIBK}(T) = (25.6 \pm 1.0) - \frac{(1200 \pm 300)}{T} \quad [16] \qquad (2)$$

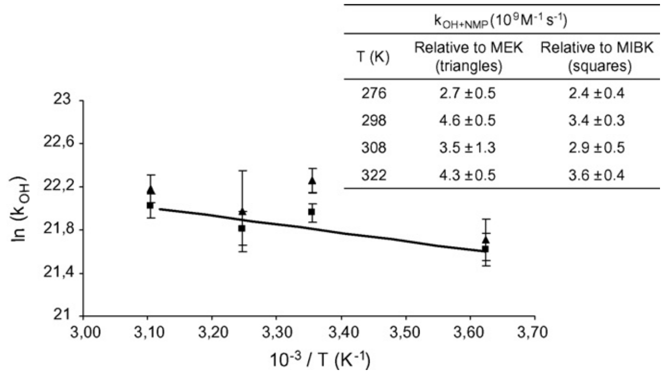
For these kinetic experiments, highly precise quantification of NMP and the two references were needed. Thus, the analysis of MEK and MIBK were performed by pre-column derivatisation with 2,4-dinitrophenylhydrazine (2,4-DNPH), HPLC (equipped with a reversed phase C_{18} column (Alltima, Alltech)) and a UV absorption at 360 nm. A tertiary eluent ($CH_3CN/H_2O/CH_3OH$) was used (isocratic at 20%/40%/40% for 3 min, then a 10 min linear gradient to 5%/25%/70%, then another 10 min linear gradient to 5%/15%/80%, hold for 6 min). Samples were prepared by removing an aliquot of 180 μL from the reactor, diluted into 800 μL of 2,4-DNPH (0.36 mg L^{-1}). These techniques gave rise to sharp peaks in chromatograms.

The 2,4-DNPH derivatisation method used for the reference compounds can not be used for NMP because no phenylhydrazone of NMP could be detected under our conditions. Direct analysis of NMP by HPLC-UV was previously performed in different experimental conditions [17–19]. Thus, the analyses of NMP used here were directly derived from this previous works and were performed by HPLC equipped with a reversed phase C_{18} column (Alltima, Alltech) and UV absorption at 212 nm. A binary methanol/water eluent was used (with a 10 min gradient from 20%/80% to 90%/10% hold for 5 min), at 1 mL min^{-1}.

Before each experiment, calibrations were carried out for each compound, in the range covering the concentrations encountered during the experiment. For MEK and MIBK, calibrations were performed from known concentrations in the aqueous solution, i.e., in the same conditions as those of the experiments.

The kinetic studies were carried out at four temperatures, between 276 and 322 K. The results are presented in Fig. 1. According the data presented, we obtain the following Arrhenius expression (3):

$$\ln(k_{OH}) = (24.4 \pm 1.1) - \frac{(760 \pm 320)}{T} \qquad (3)$$



	k_{OH+NMP} ($10^9 M^{-1} s^{-1}$)	
T (K)	Relative to MEK (triangles)	Relative to MIBK (squares)
276	2.7 ±0.5	2.4 ±0.4
298	4.6 ±0.5	3.4 ±0.3
308	3.5 ±1.3	2.9 ±0.5
322	4.3 ±0.5	3.6 ±0.4

Fig. 1. Arrhenius plot and relative rate constants (table) for the reaction of OH radical with NMP in the aqueous phase.

To our knowledge, only one previous study mentions a rate constant of $(6.9 \pm 1.2) \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ at 298 K [20]. This value is slightly higher than our data, but the reason for this is not clear. OH-oxidation of NMP is fast compared to other water soluble organic compounds, and is weakly influenced by temperature. Assuming that 15% of air contains clouds, and that $[\mathrm{OH_g}] = 10^6$ molec cm^{-3}, $[\mathrm{OH_{aq}}] = 10^{-13}$ M, one can estimate the global atmospheric life time of NMP (see details in reference [16]): the presence of clouds reduces the atmospheric life time of NMP by 13%, from 13 to 11 h. Thus, the aqueous phase OH-oxidation has an important impact on the atmospheric behaviour of NMP. Because the kinetics of the reaction is fast, special attention has to be paid to the reaction products formed.

4. Reaction products studies

To study the reaction products of NMP during its OH-oxidation in the aqueous phase, the continuous photolysis of H_2O_2 (r2) was used to produce OH radicals, because the Fenton reaction (used in the kinetic experiments) can generate artefacts on the reaction products due to the reaction of iron cations on organic radicals:

$$H_2O_2 + h\upsilon \rightarrow\ 2OH \qquad \text{(r2)}$$

The reaction took place in an aqueous phase photo-reactor, which consisted of a 450 mL Pyrex vessel. Unbuffered aqueous solutions were continuously stirred and maintained at 298(±0.2) K. The light source was a 300 W xenon arc lamp (see reference [16] for further details). The initial concentrations of NMP and H_2O_2 were 5×10^{-4} and 1×10^{-3} mol L^{-1}, respectively. The reaction products' identification and quantification were done (i) with "classic" HPLC analyses and (ii) with a new on-line system.

4.1. HPLC-UV analysis

The formation of *N*-methylsuccinimide (NMS), succinimide and 2-pyrrolidone (2P) (Table 1) was expected because it was previously observed in alkaline solutions [17] and in photocatalysis systems [19]. Moreover, the analytical method described in the kinetics part could not be used for the analysis of the reaction products because the UV absorption of NMS, succinimide and 2P at 212 nm is very low, and only NMP can be detected. Therefore, our analytical method was adjusted to optimize the detection of a mixture of NMP, NMS, succinimide and 2P with no derivative agent. The same C_{18} column as the one described above was used, with UV detection at 202 nm, and a binary eluent (80%/20% CH_3CN/H_2O) at 1 mL min^{-1}. Before each experiment, the calibration was carried out for NMP, and expected reaction products in the range covering the concentrations encountered during the experiment.

The time profiles presented in Fig. 2a show that all the expected reaction products were formed under our conditions. This figure also shows that a non-identified reaction product was formed in suspected high amounts. The plots of the reaction products' concentrations versus the concentration of NMP consumed (Fig. 2b) show that NMS and the non-identified compound were primary reaction products, whereas succinimide was a secondary one. The carbon balance of NMS production was 55 ± 1%, confirming that other primary reaction products were formed. The obtained HPLC chromatograms contained a lot of unresolved and unidentified peaks, certainly due to the formation of many other reaction products (Fig. 3). In order to identify additional reaction products, we designed a new on-line system.

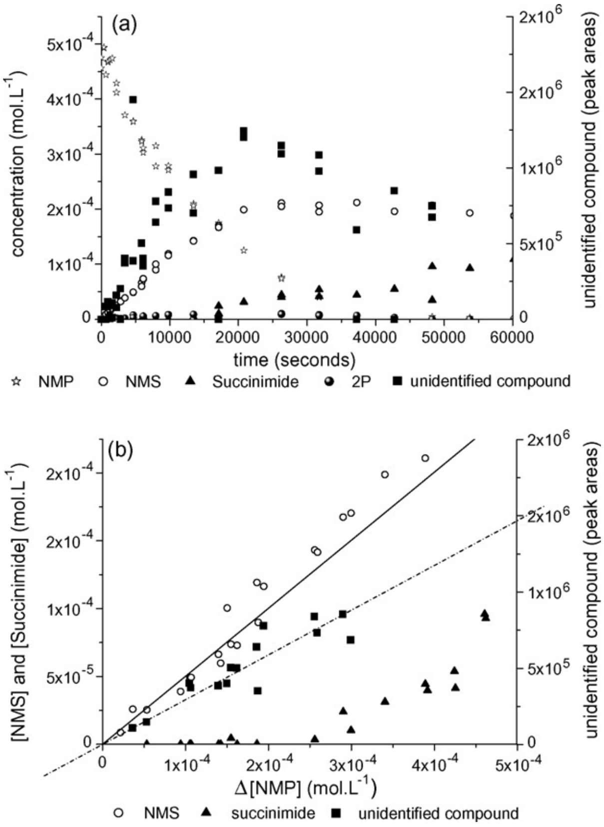


Fig. 2. HPLC analysis: (a) time profiles of NMP and reaction products during the OH-oxidation of NMP in the aqueous phase; (b) concentrations of the products (or HPLC signal in arbitrary units) versus the concentrations of the consumed NMP.

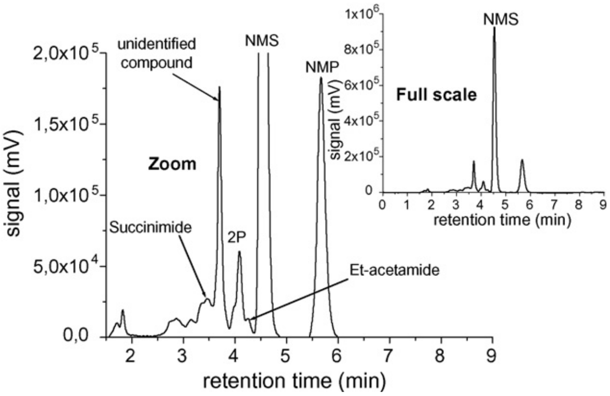


Fig. 3. Example of an HPLC chromatogram during the OH-oxidation of NMP in the aqueous phase at $t = 5$ h 46 min (20,778 s) after the injection of reactants.

Table 1
Reaction products identified in the positive mode

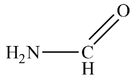
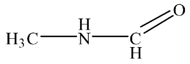
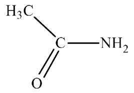
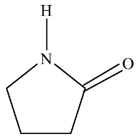
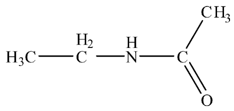
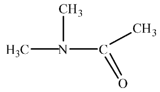
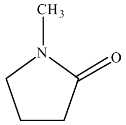
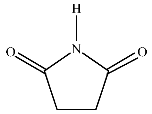
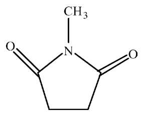
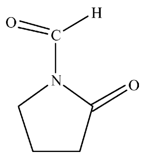
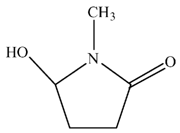
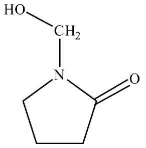
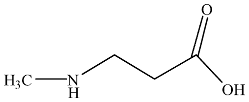
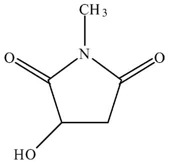
Name	Formula	m/z observed	
		$(M+H)^{+}$[a]	$(MS/MS)^{+}$ daughter ions[b]
Methylamine	$H_3C{-}NH_2$	32	
Formamide	 $H_2N{-}C(H){=}O$	46	
N-Methylformamide (NMF)	 $H_3C{-}NH{-}C(H){=}O$	60	
Acetamide	 $H_3C{-}C({=}O){-}NH_2$	60	
2-Pyrrolidone (2P)		86	69–70
N-Ethylacetamide	 $H_3C{-}CH_2{-}NH{-}C({=}O){-}CH_3$	88	57–58
Dimethylacetamide	 $H_3C{-}N(CH_3){-}C({=}O){-}CH_3$	88	
N-Methylpyrrolidone (NMP)		100 199 (NMP dimer)	58 (major) and 72
Succinimide		100	72 (major) and 58
N-Methyl succinimide (NMS)		114	86 (major)
1-Formyl-2-pyrrolidone (FP)		114	72 (major) supposed
5-Hydroxy-*N*-methylpyrrolidone (5-HNMP)		116	88 (major) and 58

Table 1 (*Continued*)

Name	Formula	*m*/*z* observed	
		$(M+H)^{+}$[a]	$(MS/MS)^{+}$ daughter ions[b]
N-Hydroxymethylpyrrolidone (NHMP)		116	73
N-Methyl-4-aminobutanoic acid		118	
2-Hydroxy-*N*-methylsuccinimid (2-HNMS)		130	
Unidentified compound[c]		132	

[a] ESI-MS^{+} scans at (M + H).

[b] ESI-MS/MS^{+} daughter ions.

[c] The $(ESI\text{-}MS)^{+}$ signal at $m/z = 132$ amu was high compared to the other unidentified compounds.

4.2. Design of the on-line system

To perform on-line analyses of the solution, the aqueous phase photo-reactor was directly connected to a mass spectrometer (MS) (without any analytical column) (Fig. 4). The MS used was a triple quadrupole (Varian Q1200L) equipped with an electrospray ionisation source (ESI). This original system permitted to avoid all the problems inherent to sampling, and stocking samples. The solution was directly injected by infusion into the MS by an HPLC pump (Varian Prostar 210). The pump flow (0.1 mL min^{-1}) was chosen to have the best compromise between maximum analytical sensitivity and minimum volume taken out the photo-reactor.

4.2.1. Analytical response

In order to obtain the shortest analytical response (which is the delay between sampling and MS analysis), we minimised the internal volume of the capillaries and that of the HPLC pump system (the mixing chamber of the pump was bypassed) (Fig. 4). We obtained a minimum delay of 9 min (Fig. 5) between the sampling from the photo-reactor and the detection by the mass spectrometer. After this delay the signal detected by the mass spectrometer is stable as long as the concentration into the photo-reactor is stable. Preliminary tests performed with this instrument have shown that if the NMP concentration in the photo-reactor decreases by dilution, the MS signal decreases with a linear response with a delay of 9 min. The shape of the signal is not a step shape, and the sampling resolution is 2 min

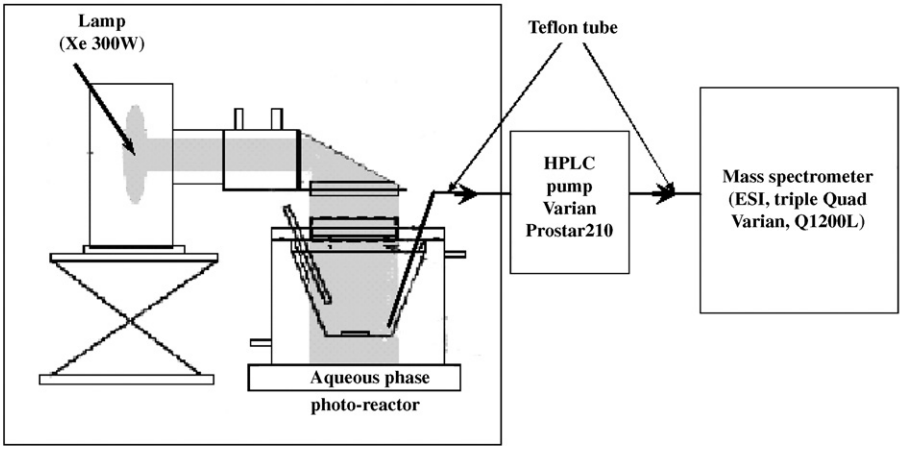


Fig. 4. Scheme of the connection between the aqueous phase photo-reactor and the mass spectrometer to perform on-line analyses. The total length of the tubings is 40 cm × 1 mm (i.d.), and the liquid volume in the pump is 0.52 mL.

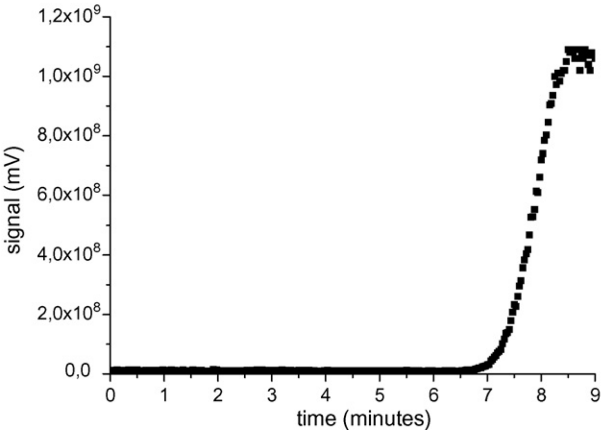


Fig. 5. Infusion time of the on-line analyser. At $t = 0$, NMP was injected into the photo-reactor. At $t = 6.5$ min, the solvent front reaches the detector, and at $t = 9$ min (infusion time), the NMP signal is stable.

(Fig. 5). This imposes to study slow reactions with the on-line system, where the variations of the concentrations are negligible (within the analytical standard deviations) over 2 min. This condition was verified for the OH-oxidation of NMP under our experimental conditions.

4.2.2. MS modes

In order to identify as many reaction products as possible, three MS modes were used during the course of the reaction: $(\text{ESI-MS})^+$, $(\text{ESI-MS})^-$ and $(\text{ESI-MS–MS})^+$ with a scan range of 20–1000 atomic mass units (amu). These three modes were alternately used during an analysis sequence of 25 min: the first mode $(\text{ESI-MS})^+$ was used during 6 min, the second one $(\text{ESI-MS–MS})^+$ during 8 min and the last one $(\text{ESI-MS})^-$ during 11 min (Fig. 6). Transition times of 3 or 4 min between each time periods were necessary for the stabilisation of the signal and the pressure inside the mass spectrometer. The duration of the transition times were made as short as possible in order to minimise the delay between two points and thus increase the resolution of the obtained time profiles of concentrations. For each mode of each sequence, the *m*/*z* signal obtained after the transition time was averaged. Due to the kinetics of the reaction, the variation of the *m*/*z* signal during one mode was negligible. Thus, each sequence gave rise to three different sampling times corresponding to the three detection modes. For an experiment of 20 h, the analysis sequence was repeated 48 times.

4.2.3. Scan range time

Another important parameter is the scan range time of the MS. In classical LC–MS working conditions, the scan range time is fast (<0.2 s) for a good peak resolution in the chromatograms. In our conditions, the compounds are not separated prior to analysis, thus we used the maximum scan range time (2 s) to raise the signal to noise ratio, and also to minimize the number of scans per sequence. Under our experimental conditions, the detection limit of NMP (corresponding to 10 times the baseline noise level) is 3.10^{-6} M.

4.2.4. Mass resolution

The mass spectrometer was equipped with a triple quadrupole. This system allowed us to perform detection in positive, negative and MS–MS mode. The mass resolution of our instrument is 1 amu. Some separate tests have shown that this resolution allows us to differentiate two compounds of molecular masses of M and M + 1 amu, respectively. Due to the mass resolution, in the results and discussions presented below, all the *m*/*z* values are rounded to the nearest whole unit.

4.2.5. Calibrations

Calibrations of the new on-line mass spectrometer were performed under our experimental conditions. Standard solutions of all the expected reaction products and NMP were infused into the MS with concentrations ranging up to 10^{-4} M. Linear responses were obtained during the calibration process for all compounds and their hydrated forms (when existing). However, it was difficult to differentiate isomers. This limitation could be compensated by the MS–MS mode detection, except when the two isomers produced the same daughter ions. An example of such interference is presented bellow for NMP and succinimide. This interference represents the most important limitation of this method.

4.3. Results

The experimental protocol revealed, for the first time to our knowledge, the time profiles of a large number of reaction products in the same time: approximately 66 different ions were obtained during the course of the reaction (40 cations in the $(\text{ESI-MS})^+$ mode (Fig. 7a), and 26 anions in the $(\text{ESI-MS})^-$ mode (Fig. 7b)). An excellent reproducibility of the mass spectra was observed through three experiments. Among the 66 ions observed, 24 lead to the identification of the corresponding compounds as discussed in details below (Tables 1 and 2). NMP was

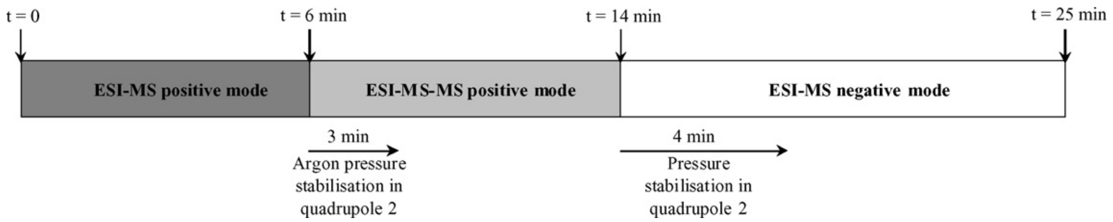


Fig. 6. Scheme of the 25 min operation cycle used with the on-line analyser during the OH-oxidation of NMP in the aqueous phase. The cycle was repeated 48 times, to cover 20 h of a reaction run.

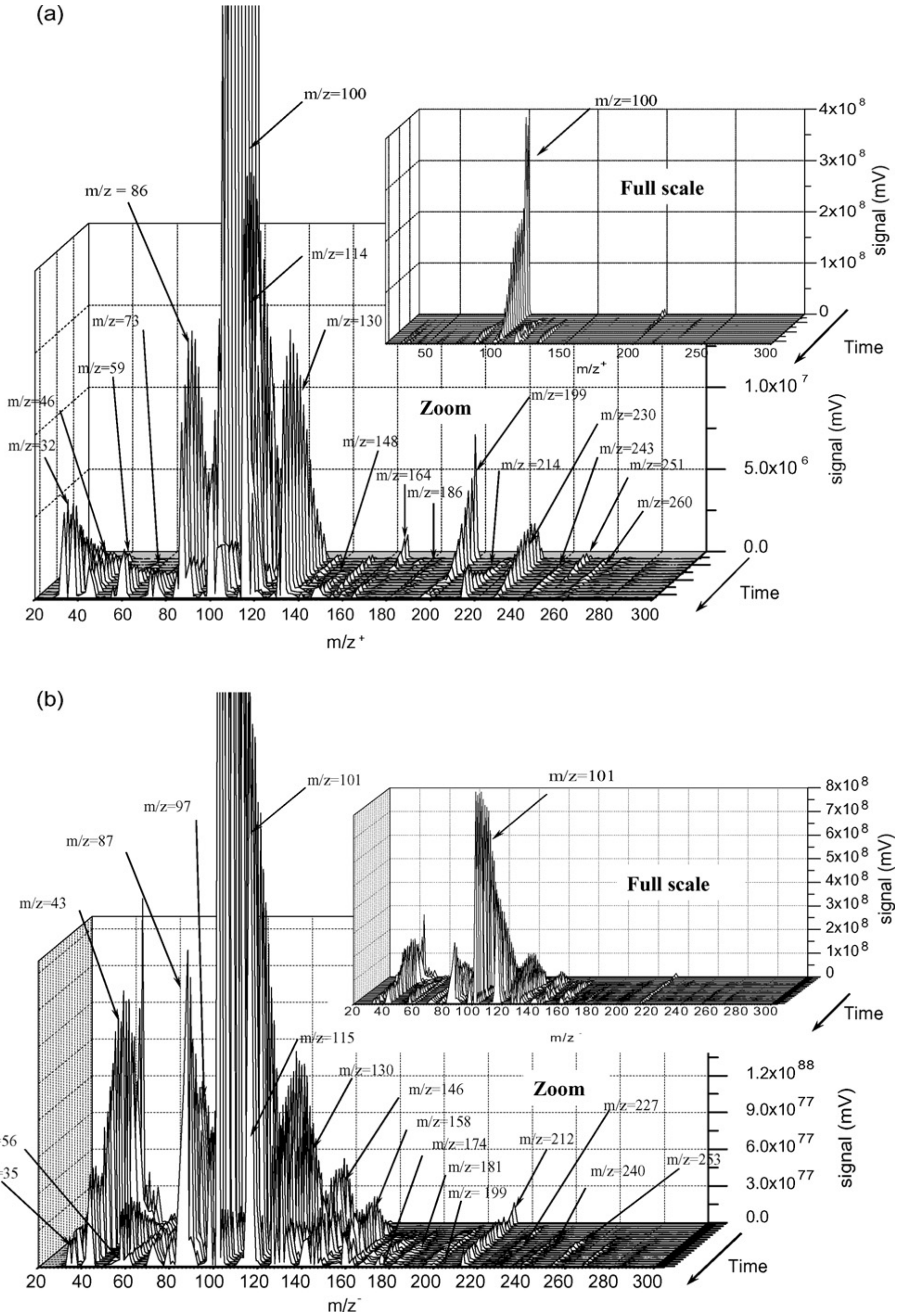


Fig. 7. Full scale and zoom of 3D plots of the MS signal vs. mass and time during the OH-oxidation of NMP in the aqueous phase (scan range 20–1000 amu of which 20–300 amu is shown here): (a) in the positive mode, and (b) in the negative mode. See Tables 1 and 2 for the identification of the observed masses.

detected in positive mode at $m/z = 100$ amu: one can see in Fig. 7a and b the decrease of its signal with time, and the simultaneous formation of several ions. Some of the ions show a reactive time profile, i.e., after a fast increase, their concentrations reach a maximum then decrease, certainly due to the reaction of the corresponding compounds with OH radicals during the course of the reaction (see, for example, $(\text{ESI-MS})^+ = 86$, 114 and 130 amu or $(\text{ESI-MS})^- = 43$ and 115 amu in Fig. 7). Although the scan was performed up to 1000 amu, no signal was observed above 300 amu. Finally, in both modes, one can observe the formation of ions for which mass intervals range from 13 to 18 amu (Fig. 7a and b): this observation is discussed below.

4.3.1. Discussion and identification of the main reaction products

4.3.1.1. m/z = 100 and 199 amu. NMP was detected at $(\text{ESI-MS})^+ = 100$ amu. Interestingly, its dimer was detected at $(\text{ESI-MS})^+ = 199$ amu with a weaker signal. This dimer was not the result of a reaction product in the aqueous phase because it was also observed during the analysis of standard solutions. Thus, it

Table 2
Reaction products identified in the negative mode

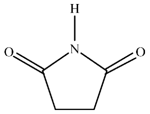
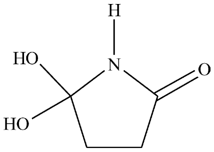
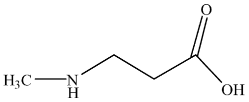
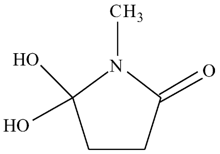
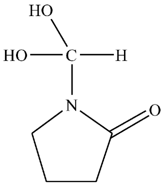
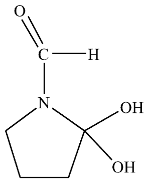
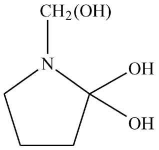
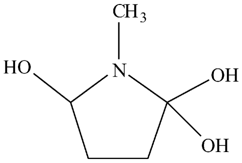
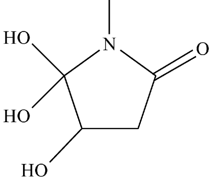
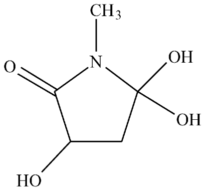
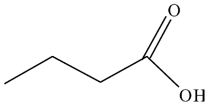
Name	Formula	*m/z* observed	
		$(M-H)^{-a}$	$(M-H+H_2O)^{-b}$
Succinimide		97[c]	
Hydrated Succinimide			115[c]
N-Methyl-4-aminobutanoic acid		116	
Hydrated *N*-methyl succinimide (NMS)			130
Hydrated 1-formyl-2-pyrrolidone (FP)	 or 		130
Hydrated *N*-hydroxymethylpyrrolidone (NHMP)			132
Hydrated 5-hydroxy-*N*-methylpyrrolidone (5-HNMP)			132
Hydrated 2-hydroxy-*N*-methylsuccinimide (2-HNMS)	 or 		146

Table 2 (*Continued*)

Name	Formula	*m/z* observed	
		$(M-H)^-$[a]	$(M-H+H_2O)^-$[b]
Butanoic acid		87	
Unidentified compounds[d]		43 101 148	

[a] ESI-MS$^-$ scan at (M − H).

[b] ESI-MS$^-$ scans of hydrated ions corresponding to (M − H).

[c] Succinimide was identified at $(M-2H)^-$ and its hydrate was identified at $(M-2H+H_2O)^-$ after verification with standard solutions (see text).

[d] The (ESI-MS)$^-$ signals at *m/z* = 43, 101 and 148 amu were high compared to the other unidentified compounds.

was probably formed in the electrospray unit of the mass spectrometer.

Time profiles of the NMP signal in HPLC-UV and MS show a good agreement up to time = 8000 s (Fig. 8). After this time, the MS signals at *m/z* = 100 show a significant shoulder up to 22,000 s. Because no separation of the products was performed on the on-line system, the observed shoulder can be explained by the formation of a reaction product generating ions of the same mass as NMP. Succinimide, which was identified as a reaction product (in HPLC-UV analyses), produced ions at *m/z* = 100 amu with the on-line system. To identify separately NMP and succinimide, the analyses were carried out using the (ESI-MS–MS)$^+$ mode. The (ESI-MS–MS)$^+$ analysis of standard solutions of the two compounds have revealed the formation of the same daughter ions (58 and 72 amu) in reverse proportions (Table 3). Fortunately, standard solutions of succinimide showed that this compound and its hydrate can be detected in (ESI-MS)$^-$ mode at *m/z* = 97 and 115 amu (Table 2), and thus can be distinguished from NMP (Fig. 9). One can note that succinimide (molecular mass of 99 g mol^{-1}) was detected at *m/z* = 97 amu which corresponds to the loss of *two* hydrogen atoms. This is surprising, considering the chemical structure of this compound, and the resolution of the instrument (1 amu). The same kind of observation was performed on the hydrated form of succinimide: its molecular mass is 117 g mol^{-1}, and it was observed at

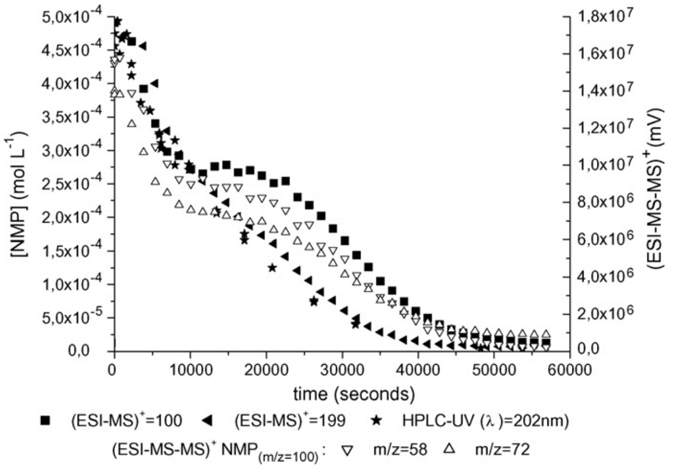


Fig. 8. Comparison of NMP time profiles obtained with HPLC-UV and with MS analysis. The MS signals of NMP are (ESI-MS)$^+$ at *m/z* = 100 and 199 amu, and daughter ions of *m/z* = 100 amu at 58 and 72 amu.

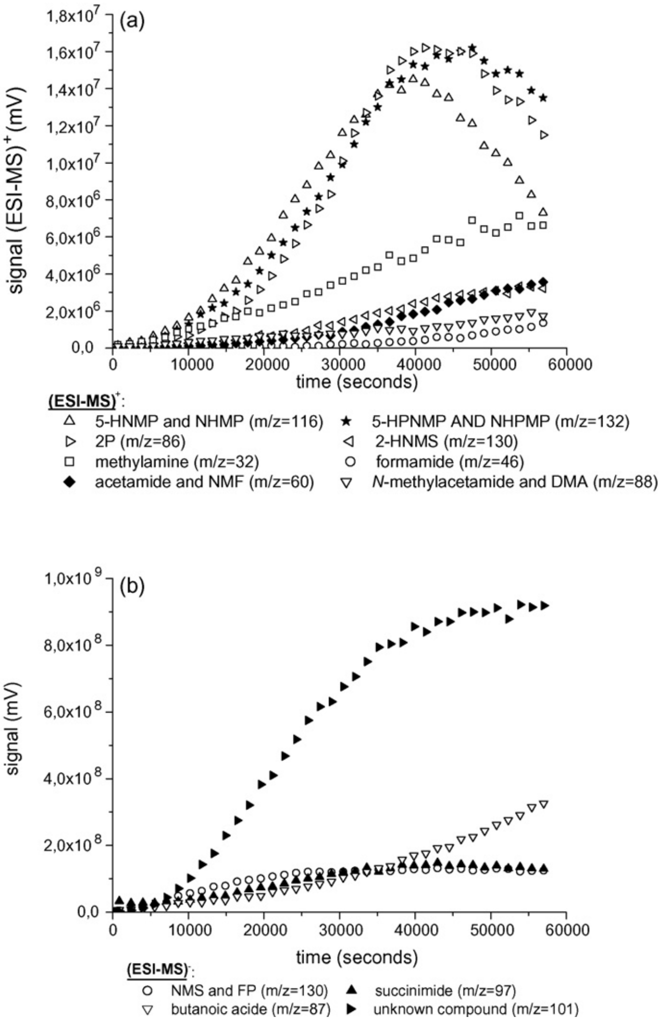
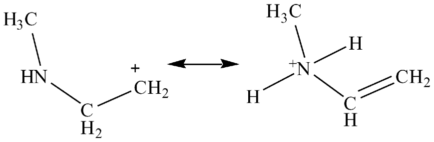
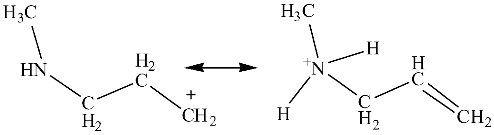
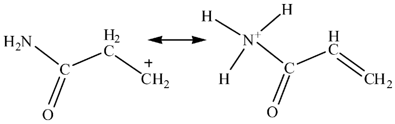
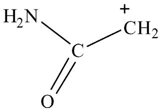
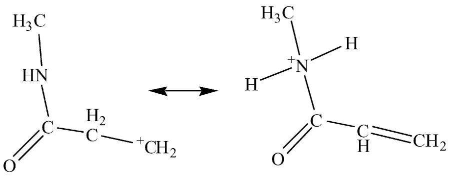
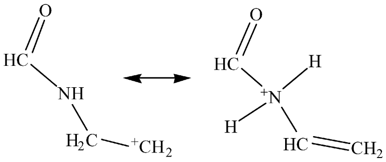
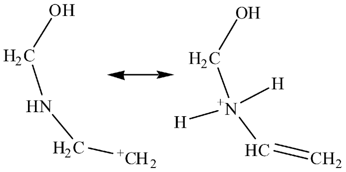
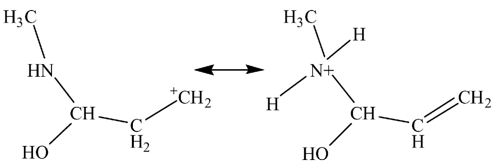
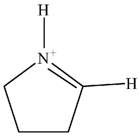


Fig. 9. Time profiles of reaction products' signals during the OH-oxidation of NMP in the aqueous phase: (a) (ESI-MS)$^+$ scans and (b) (ESI-MS)$^-$ scans.

Table 3
(ESI-MS–MS)$^+$ fragmentation schemes of the main reaction products of OH-oxidation of NMP in the aqueous phase

Name	Daughter cations	Neutral loss	*m*/*z* observed	Identification
NMP		$H_2C{=}C{=}O$	58 (major)	Standard solution
		CO	72 (minor)	
Succinimide		CO	72 (major)	Standard solution
		$H_2C{=}C{=}O$	58 (minor)	
NMS		CO	86	Standard solution
FP		$H_2C{=}C{=}O$	72	Analogy with succinimide
NHMP		$H_2C{=}C{=}O$	73	Analogy with NMP
5-HNMP		CO	88	Standard solution
2P		1/2 O_2	70	Standard solution

$m/z = 115$ amu. The reasons for these observations are unclear. The time profiles of succinimide obtained by HPLC-UV were in very good agreement with those obtained at $m/z = 97$ amu in the $(ESI\text{-}MS)^-$ mode with the on-line mass spectrometer. This good correlation contributes to the validation of the new on-line system.

4.3.1.2. m/z = 114. One of the main reaction product identified in HPLC-UV was *N*-methylsuccinimide (NMS). Standard solutions of NMS have shown that it is detected in $(ESI\text{-}MS)^+$ at $m/z = 114$ amu, and its hydrate is detected in $(ESI\text{-}MS)^-$ at $m/z = 130$ amu. However, an excessive carbon balance (≈120%) was obtained with the signals at $m/z = 114$ amu (calibrated with standard solutions of NMS), in disagreement with the $55 \pm 1\%$ carbon balance obtained by HPLC-UV (see the above section). Therefore, the formation of another reaction product at $m/z = 114$ (in $(ESI\text{-}MS)^+$) and 130 amu (in $(ESI\text{-}MS)^-$) was suspected. Aschmann and Atkinson [14] have shown that 1-formyl-2-pyrrolidone (FP) is an important primary reaction product of OH-oxidation of NMP in gas-phase. The molecular weight of FP ($113\ g\ mol^{-1}$) is equal to that of NMS, thus it can also be detected at $m/z = 114$ in $(ESI\text{-}MS)^+$. The $(ESI\text{-}MS\text{–}MS)^+$ scans of mass $m/z = 114$ during the course of our experiments have shown the formation of two daughter ions, at $m/z = 86$ and 72 amu. The analyses of standard solutions of NMS have shown that only the daughter ion 86 amu is obtained. FP is not commercially available, so we could not perform separate tests for this compound. However, by analogy with NMP, succinimide, and NMS fragmentation in $(ESI\text{-}MS\text{–}MS)^+$, the major fragmentation pathway of FP should include the loss of $CH_2{=}C(O)$ (Table 3). Such a fragmentation leads to the formation of a major daughter ion at $m/z = 72$ amu, thus confirming that FP was formed in our experiments of OH-oxidation of NMP in the aqueous phase. It is thus likely that FP was the unidentified primary reaction product detected in HPLC-UV (Fig. 2).

4.3.1.3. m/z = 116. In their review, von Sonntag and Schuchmann [21] have shown that concomitant formation of hydroxycarbonyl and dicarbonyl compounds can occur during the OH-oxidation of organic compounds in the aqueous phase. Moreover, Friesen et al. [19] observed the concomitant formation of NMS (dicarbonyl) and 5-hydroxy-*N*-methylpyrrolidone (hydroxycarbonyl: 5-HNMP which molecular weight is $115\ g\ mol^{-1}$) during the photocatalysis of NMP in the aqueous phase. Therefore, we suspected the formation of 5-HNMP (concomitant to NMS), and that of *N*-hydroxymethylpyrrolidone (NHMP) (concomitant to FP). In our experiments, a signal in $(ESI\text{-}MS)^+$ at $m/z = 116$ amu was detected (Fig. 7a and 9a). The $(ESI\text{-}MS\text{–}MS)^+$ scans of the parent mass of 116 amu revealed the formation of two daughter ions at $m/z = 88$ and 73 amu. Tests with standard solutions of NHMP have shown that it is detected by our system in $(ESI\text{-}MS)^+$ at $m/z = 116$ amu, with a daughter ion at $m/z = 73$ amu. Furthermore, the hydrated form of this compound is also detected in $(ESI\text{-}MS)^-$ at $m/z = 132$ in both standard and experimental solutions (Table 3). Although 5-HNMP is not commercially available, by analogy with the MS–MS fragmentation pathways of NMP, succinimide, FP and NHMP, the major MS–MS fragmentation pathway of 5-HNMP should be the loss of CO, leading to a daughter ion at $m/z = 88$ amu (Table 3). It is in good agreement with our observations and it confirms the formation of 5-HNMP. Thus the formation of NHMP and 5-HNMP during the OH-oxidation of NMP in the aqueous phase is confirmed.

4.3.1.4. m/z = 132. The formation of a compound detected in $(ESI\text{-}MS)^+$ mode at $m/z = 132$ amu could correspond to the formation of an organic hydroperoxyde (Figs. 7a and 9a). The presence of such compounds during the OH-oxidation of organic compounds in the aqueous phase was suggested by Zegota et al. [22] and confirmed by recent studies ([9,10,23]). Finally, Drago and Riley [24] have characterised an organic hydroperoxyde (5-hydroperoxo-1-methyl-2-pyrrolidone or 5-HPNMP) at $m/z = 132$ during the oxidation of *N*-alkylamides in the aqueous phase. It is likely that the signal at $m/z = 132$ amu corresponds to more than one compound. Unfortunately, commercial standards of hydroperoxides are not available, so we cannot propose any $(ESI\text{-}MS\text{–}MS)^+$ fragmentation pathways in order to identify the corresponding compounds.

4.3.1.5. m/z = 130. Carnerup et al. [18] have observed the formation of 2-hydroxymethylsuccinimide (2-HNMS) at $m/z = 130$ (Table 1 and Fig. 9a) in biodegradation studies. The presence of a signal corresponding to this mass was observed in our experiments in $(ESI\text{-}MS)^+$, and it may correspond to the formation of 2-HNMS.

4.3.1.6. m/z = 86. The formation of 2-pyrrolidone (2P) was suggested by [17,19]. We observed its formation in $(ESI\text{-}MS)^+$ at $m/z = 86$ amu (Figs. 7a and 9a), with a daughter ion (in $(ESI\text{-}MS\text{–}MS)^+$ mode) at $m/z = 70$ (Table 3). The identification was performed with standard solutions of 2P.

4.3.1.7. Low mass range. The formation of smaller compounds corresponding to non-cyclic compounds was observed in both positive and negative modes (Tables 1 and 2 and Fig. 9). It may correspond to methylamine, formamide, detected in $(ESI\text{-}MS)^+$ at $m/z = 32$ and 46 amu, respectively, which were confirmed with standard solutions. *N*-Methylformamide (NMF) and acetamide (detected in $(ESI\text{-}MS)^+$ at $m/z = 60$ amu) and *N*-ethylacetamide and dimethylacetamide (DMA) (detected in $(ESI\text{-}MS)^+$ at $m/z = 88$ amu) may be produced during the OH-oxidation of NMP. Nevertheless, the subsequent MS–MS fragmentation of these compounds was too busy to distinguish each compound.

4.3.1.8. High mass range. In our experiments, the formation of compounds with higher molecular weight than NMP was observed (Fig. 7a and b). Such observations were performed in both detection modes up to 300 amu with mass intervals ranging from 13 to 18 amu. For example, in the positive mode, the cations observed above 164 amu are at $m/z = 186$, 199, 214, 230, 243 and 260 amu, corresponding to mass spaces of

13, 15, 16, 13 and 17 amu. In the negative mode, the anions observed above 174 amu are at $m/z = 181$, 199, 212, 227 and 240 amu, corresponding to mass spaces of 18, 13, 15 and 13 amu. The possible reasons for these observations are examined below.

- The formation of dimers of some of the reaction products during the ionisation process into the electrospray can occur similarly to the dimer of NMP (detected at $m/z = 199$ amu). However, standard solutions of NMS, succinimide, NHMP and 2P did not show any significant dimer formation. Thus,

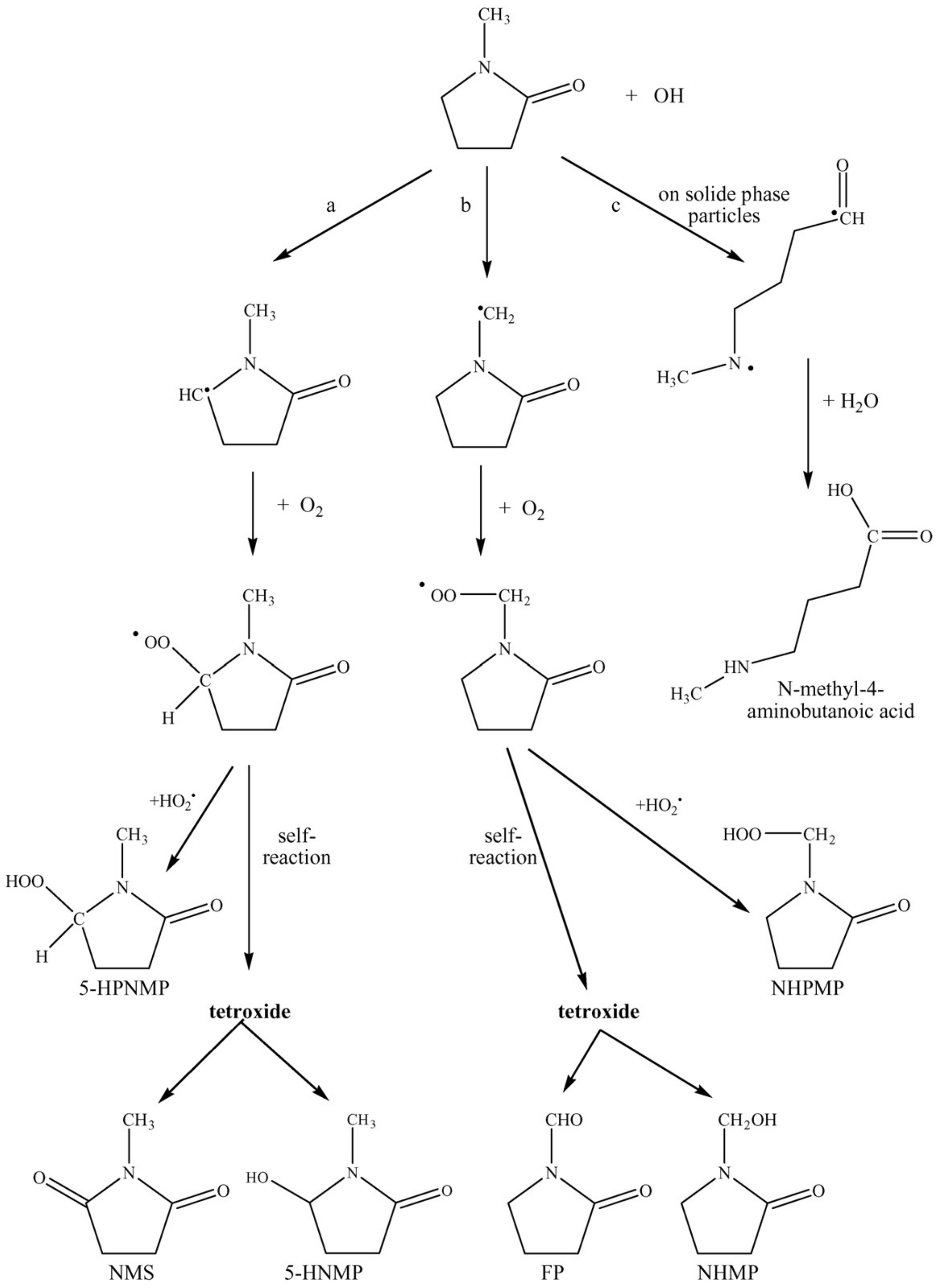


Fig. 10. Suggested mechanism of the OH-oxidation of NMP in the aqueous phase.

the formation of such dimers does not fully explain the observations.

- The increasing oxidation level of NMP leads to the formation of more and more oxidized molecules, with higher molecular masses. For example, the formation of 2-HNMS corresponds to the OH-oxidation of NMS, which corresponds to the OH-oxidation of NMP. In this case, the highest oxidation level should be detected at $m/z = 156$ amu in (ESI-MS)$^+$ mode, and the corresponding hydrated form at $m/z = 244$ amu in (ESI-MS)$^-$ mode. Thus, this cannot fully explain masses detected up to 300 amu.
- Polymerisation or oligomerisation processes can occur. Such phenomena were previously suggested by Blando and Turpin [25] and observed for the first time in the aqueous phase by Gelencsér et al. [6] who studied the reactivity of 3,5-dihydroxybenzoic acid. The formation of polymers during the aqueous phase reactivity of organic compounds was also explored and confirmed by different atmospheric multiphase models [26,27]. In our study, the detection of high molecular compounds (compared to NMP) up to 300 amu, with mass intervals ranging from 13 to 18 amu can be the consequence of the formation of molecular aggregates by addition of small carbonyls (and their hydrated forms) or acid compounds (formed during the course of the reaction) on the primary reaction products and/or on organic radicals.

4.3.2. Chemical mechanisms

Based on the identified reaction products, we suggest a mechanism of OH-oxidation of NMP in the aqueous phase, under tropospheric conditions. The reaction can proceed via three different pathways (Fig. 10).

4.3.2.1. Pathway a. The attack of OH radicals proceeds via a hydrogen abstraction on the CH_2 group adjacent to the amine group of NMP [17,19]. This leads to the formation of an alkyl radical which reacts with dissolved oxygen to form a peroxy radical. By analogy with the aqueous phase behaviour of other peroxy radicals [21], this radical can self-react to form a tetroxide, which rapidly decomposes into NMS and 5-HNMP. The HPLC-UV analysis of NMS allowed us to determine that the importance of this pathway is 55 ± 1%. The peroxy radical can also react with $HO_2^\bullet$ to form an organic hydroperoxyde, the 5-HPNMP which decomposes slowly to form NMS as proposed by Friesen et al. [19].

4.3.2.2. Pathway b. The attack of OH radicals proceeds via a hydrogen abstraction on the methyl group of NMP. This pathway leads to the formation of another alkyl radical, which then reacts with dissolved oxygen to form a peroxy radical. This peroxy radical can self-react to form a tetroxide which rapidly decomposes, leading to the formation of FP and NHMP. The peroxy radical can react with $HO_2^\bullet$ to form an organic hydroperoxyde (NHPMP). Further reactivity of FP, NHMP and/or NHPMP should lead to the break of the C–N bond and to the formation of 2P detected in our experiments as a secondary reaction product. This second pathway was previously mentioned by Friesen et al. [19] only briefly, and our study is the first experimental evidence for this pathway, to our knowledge.

4.3.2.3. Pathway c. This pathway is more speculative than pathways a and b. An analogous pathway was mentioned by Horikoshi et al. [28], who performed OH-oxidation of 2P in the aqueous phase in the presence of solid phase TiO_2. In our conditions, i.e., in the absence of particles, this pathway may not occur. However, this pathway should be considered under real tropospheric conditions as solid phase particles of various origins are present in aqueous droplets. It proceeds via a ring opening mechanism, leading to the formation of *N*-methyl-4-aminobutanoic acid.

5. Conclusion

The reactivity of OH radicals with NMP in the aqueous phase under tropospheric conditions was investigated in this work. The kinetic results show that OH-oxidation of NMP is fast compared to that of other water soluble organic compounds, and thus should induce modifications of the composition of water droplets, due to the reaction products formed. A new experimental technique was developed to study the aqueous phase OH-oxidation of NMP. A mass spectrometer was directly coupled with an aqueous phase photo-reactor, thus providing an on-line analysis of the solution. The mass spectrometer was a triple quadrupole equipped with an electrospray ionisation source (ESI). It was operated in the (ESI-MS)$^+$, (ESI-MS)$^-$ and (ESI-MS–MS)$^+$ modes, with a scan range from 20 to 1000 amu. The results proved that this experimental technique was highly promising, as it allowed us to detect the formation of about 66 different ions, of which 24 corresponded to identify reaction products. Comparison with results obtained with HPLC-UV off-line analyses showed good agreement for compounds identified with both systems, thus validating the new on-line system. The main oxidation products identified were succinimide, *N*-methylsuccinimide (NMS), formylpyrrolidone (FP), *N*-hydroxymethylpyrrolidone (NHMP), 5-hydroxy-*N*-methylpyrrolidone (5-HNMP), 2-pyrrolidone (2P), methylamine, formamide, acetamide, *N*-methylformamide, *N*-ethylacetamide and dimethylacetamide. The time profiles of these compounds were obtained, and a chemical mechanism of OH-oxidation of NMP in the aqueous phase was suggested. Two main reaction pathways (a and b) were explored, leading to the formation of the identified primary reaction products. Pathways a and b correspond to hydrogen atom abstraction on, respectively, the CH_2 and CH_3 groups next to the hetero-atom of the NMP molecule. Each pathway gave rise to the concomitant formation of a dicarbonyl and a hydroxycarbonyl compound: NMS and 5-HNMP were formed in pathway a, and FP and NHMP were formed in pathway b.

The on-line mass spectrometer also allowed us to observe the formation of high molecular compounds (compared to the parent compound NMP), i.e., up to 300 amu, with mass intervals ranging from 13 to 18 amu. These high molecular compounds are probably the result of the formation of molecular aggregates by addition of small carbonyl or acid compounds (formed during the course of the reaction) on the primary reaction products and/or on organic radicals. This needs more experimental investigations to be confirmed.

The on-line analysis of reaction products in the aqueous phase was investigated here for the first time to our knowledge, and the study of the reactivity of NMP has validated this new system. It has shown some essential advantages: it permitted to avoid all the problems inherent to sampling, and stocking samples; it permitted the detection of a large number of reaction products, and to obtain their time profiles. A few limitations are inherent to the system: the sampling resolution is 2 min, imposing to study slow reactions; and isomers can be difficult to differentiate. Knowing these advantages and limitations, the on-line system can now be used to study the reactivity of other organic compounds in water.

Acknowledgement

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References

[1] B. Ervens, S. Gligorovski, H. Herrmann, Phys. Chem. Chem. Phys. 5 (2003) 1811–1824.
[2] H. Herrmann, Chem. Rev. 103 (2003) 4691–4716.
[3] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 513–886.
[4] NIST, NDRL/NIST Solution Kinetics Database on the Web, NIST Standard Reference Database 40, A Compilation of Kinetics Data on Solution-Phase Reactions, 2002 (http://www.kinetics.nist.gov/solution/index.php).
[5] E. Chevallier, Ph.D. thesis, Université Paris 7, Paris, 2004.
[6] A. Gelencsér, A. Hoffer, G. Kiss, E. Tombacz, R. Kurdi, L. Bencze, J. Atm. Chem. 45 (1) (2003) 25–33.
[7] W.J. Mc Elroy, S.J. Waygood, J. Chem. Soc. Faraday Transcriptions 87 (10) (1991) 1513–1521.
[8] A. Monod, A. Chebbi, R. Durand-Jolibois, P. Carlier, Atm. Env. 34 (2000) 5283–5294.
[9] K. Stemmler, U. von Gunten, Atm. Env. 34 (25) (2000) 4253–4264.
[10] K. Stemmler, U. von Gunten, Atm. Env. 34 (25) (2000) 4241–4252.
[11] Basf, *N*-Methylpyrrolidone, 2006 (http://www.basf.com/diols/bcdiolsnmp.html).
[12] Sage Solvent Alternatives Guides, *N*-Methylpyrrolidone general information, 2006 (http://clean.rti.org/alt.cfm?id=nmp&cat=gi).
[13] W.P.L. Carter, D. Luo, I.L. Malkina, E.C. Tuazon, S.M. Aschmann, R. Atkinson, Report to ARCO Chemical Corporation, 1996.
[14] S.M. Aschmann, R. Atkinson, Atm. Env. 33 (1999) 591–599.
[15] J. Hine, P.K. Moorkerjee, J. Org. Chem. 40 (1975) 293–298.
[16] A. Monod, L. Poulain, S. Grubert, D. Voisin, H. Wortham, Atm. Env. 39 (2005) 7667–7688.
[17] H.L. Campbell, B.A. Striebig, Env. Sci. Technol. 33 (11) (1999) 1926–1930.
[18] M.A. Carnerup, B. Åkesson, B.A.G. Jönsson, J. Chromatogr. B 761 (2001) 107–113.
[19] D.A. Friesen, J.V. Headley, C.H. Langford, Env. Sci. Technol. 33 (18) (1999) 3193–3198.
[20] D. Rousse, Ph.D. thesis, Université Claude Bernard, Lyon, 2005.
[21] C. von Sonntag, H.-P. Schuchmann, Peroxyl Radicals in Aqueous Solution, John Wiley & Sons Ltd., Chichester, England, 1997.
[22] H. Zegota, M.N. Schuchmann, D. Schulz, C.V. Sonntag, Zeitschrift für Naturforschung 41b (1986) 1015–1022.
[23] L. Poulain, Ph.D. thesis, Université de Provence, Marseille, 2005.
[24] R.S. Drago, R. Riley, J. Am. Chem. Soc. 112 (1990) 215–218.
[25] J.D. Blando, B.J. Turpin, Atm. Env. 34 (10) (2000) 1623–1632.
[26] B. Ervens, G. Feingold, S.M. Kreidenweis, J. Geophys. Res. 110 (2005) D18211, doi:10.1029/2004JD005634.
[27] A. Gelencser, Z. Varga, Atmos. Chem. Phys. 5 (2005) 2823–2831.
[28] S. Horikoshi, H. Hidaka, N. Serpone, J. Photochem. Photobiol. A: Chem. 138 (1) (2001) 69–77.