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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 ($\ln(k_{OH}) = (24.4 \pm 1.1) - (760 \pm 320)/T$), 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

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]):

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

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

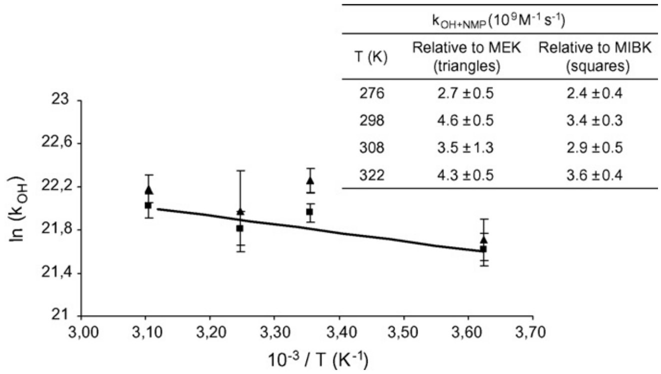
For these kinetic experiments, highly precise quantification of NMP and the two references were needed. Thus, the analysis of MEK and MIBK were performed by pre-column derivatisation with 2,4-dinitrophenylhydrazine (2,4-DNPH), HPLC (equipped with a reversed phase C_{18} column (Alltima, Alltech)) and 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.