J. Braz. Chem. Soc., Vol. 16, No. 2, 270-274, 2005.
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0103 - 5053 $6.00+0.00

Short Report

Membrane Introduction Mass Spectrometry Applied to the Monitoring of Chloroform Degradation by Hypochloride in Acidic Aqueous Medium

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A técnica MIMS (Membrane Introduction Mass Spectrometry) foi utilizada para investigar a degradação de clorofórmio em meio aquoso ácido por hipoclorito de sódio. Através dos resultados experimentais uma sequência reacional para a degradação de $CHCl_3$ até CO_2 e HCl foi sugerida. Além disso, foi também proposta a formação de fosgênio ($COCl_2$) como uma espécie intermediária em tais condições experimentais.

Membrane Introduction Mass Spectrometry (MIMS) was used to investigate chloroform degradation in acidic aqueous medium by sodium hypochloride (NaClO). From the experimental results a reaction sequence for the complete degradation of $CHCl_3$ to CO_2 and HCl was suggested. Furthermore, it was also proposed the formation of phosgene ($COCl_2$) as a transient species under these experimental conditions.

Keywords: membrane introduction mass spectrometry, chloroform degradation monitoring, sodium hypochloride, reaction mechanism, transient species

Introduction

Membrane Introduction Mass Spectrometry (MIMS)[1] has became one of the simplest, fastest, and sensitive techniques for the analysis of volatile[2,3] and semi-volatile[4-6] organic compounds in water as well as in other matrixes such as air and soil.[7-13] In this technique volatile and semi-volatile organic compounds permeate hydrophobic membranes, usually polydimethylsiloxanes (PDMS), preferentially to water and other polar substances.[14-16] MIMS can be applied to real-time and *in-situ* monitoring[14,16-18] of chemical processes, such as: (a) conversion of chlorine to chloramines, an environmentally relevant reaction;[19-21] (b) chlorination of phenol and related compounds, models of humic substances, by sodium hypochloride;[22] (c) oxidation of benzene derivatives by Fenton's reagent;[23] (d) photolysis of aryl methyl ester in aqueous and aqueous-methanolic solutions;[24] (e) hydrolysis of epichlorohydrin, a significant compound in the polymer industry;[25] (f) catalytic hydrodechlorination of aromatic chlorides, an important process to treat organochloro compounds.[26]

Chloroform is a suspected bladder, rectum and liver carcinogen agent in humans.[27] Because of that, several studies have been performed in order to find a method for removing chloroform from drinkable or waste water, with a minimum environmental impact. Thus, the use of high[28] or low-energy[29] electron beam process has been shown to be an effective way to control chloroform in water treatment stations. Another study involves the employment of a promising photocatalytic decomposition using TiO_2.[30,31] In an alternative approach, it was verified that chloroform can be decomposed by an anaerobic bacteria, *Acetobacterium woodii*, with excellent results.[32] Furthermore, activated carbon has been employed to eliminate chloroform from water owing to its high adsorption efficiency.[18]

It is well-known that the degradation of organic material by sodium hypochloride, commonly used in water treatment stations, can produce chloroform as the final product.[22] Thus, it is of high interest to verify if chloroform itself could be degraded by hypochloride. Hence, in this paper MIMS was used by the first time to monitor the reaction between chloroform and sodium hypochloride in acidic aqueous medium aiming to detect possible transient species as well as to furnish significant mechanistic information about such a process.

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Experimental

The chemicals (chloroform, sodium hypochloride) were purchased from Merck and used without further purification. The experiments were carried out on a HP 5989A II mass spectrometer equipped with a flow-through type membrane probe mounted near to the ion source. The details of the probe construction are described elsewhere.[33] A 250 μm silicone membrane (Dow Corning Silastic 500-3) with exposed area of 4 mm^2 was used. Mass spectra were obtained by electron ionization at 70 eV. The EI fragment ions of *m/z* 83 and 63 were continuously monitored during the reaction of chloroform and hypochloride (see details later in this paper). In a typical experiment, the membrane probe was connected to the mass spectrometer as illustrated in Figure 1. Chloroform aqueous solution (100 mL at 0.5 mmol L^{-1}) was pumped (by a piston pump Intralab model 2010) through the membrane probe at 5 mL min^{-1} and returned to the reaction flask. Under stirring and constant temperature kept at 25±1 °C by a water recirculating bath, 5 mL of sodium hypochloride 0.7 mol L^{-1} (3.5 mmol) were added to the solution which increased its pH to around 10. Subsequently, 5 mL of HCl 0.1 mol L^{-1} were put into this solution and the MIMS monitoring was performed as previously described. No precaution was taken to remove oxygen from the system.

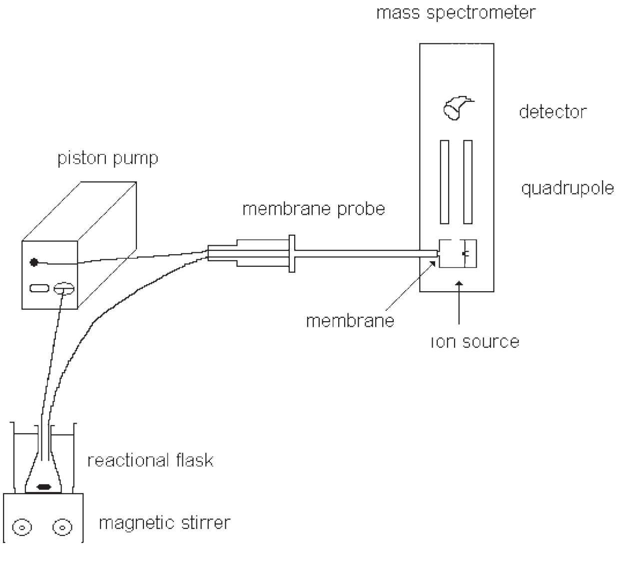

Figure 1. Schematic representation of the MIMS system.

Results and Discussion

Chloroform reaction with sodium hypochloride (NaClO)

The MIMS profile obtained for the reaction between chloroform and sodium hypochloride (NaClO) is shown in Figure 2. Note that just after the addition of NaClO and HCl the characteristic chloroform EI fragment ion of *m/z* 83 starts to decrease and reaches a minimum intensity in a reaction time of *ca.* 7 minutes. Thus, this result indicates that hypochloride is an efficient reactant to promote a quick and total degradation of chloroform. It must be mentioned, however, that in the absence of HCl there is no consumption of chloroform indicating that an acidic medium is essential for the occurrence of such a reaction.

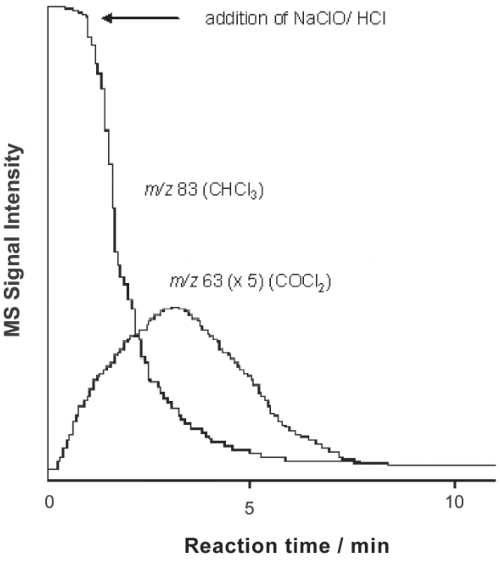

Figure 2. MIMS profile for the reaction between $CHCl_3$ and NaClO in an aqueous acidic medium.

Intermediates detection

MIMS monitoring also revealed the appearance of prominent fragment ions (98/100 and 63/65) during the chloroform degradation process, as shown by the total mass spectrum obtained, for instance, in a reaction time of *ca.* 3 minutes (Figure 3).

Based on these results and on the comparison with the appropriate EI mass spectrum,[34] the formation of phosgene ($COCl_2$) in such reaction pot was undoubtedly attributed. To further confirm the presence of phosgene as a degradation product in these reaction conditions, the relative intensities of the isotopomeric EI fragments were analyzed, considering the ^{35}Cl and ^{37}Cl isotope abundances. The results, which can be observed in Figure 3, are displayed in Table 1. The excellent agreement between the calculated and observed relative intensities of the EI fragments containing two ($[COCl_2]^{+\bullet}$) and one ($[COCl]^+$) chlorine atoms, constitutes additional evidence for the alleged formation of phosgene.

Furthermore, Figure 2 shows that the intensity of the

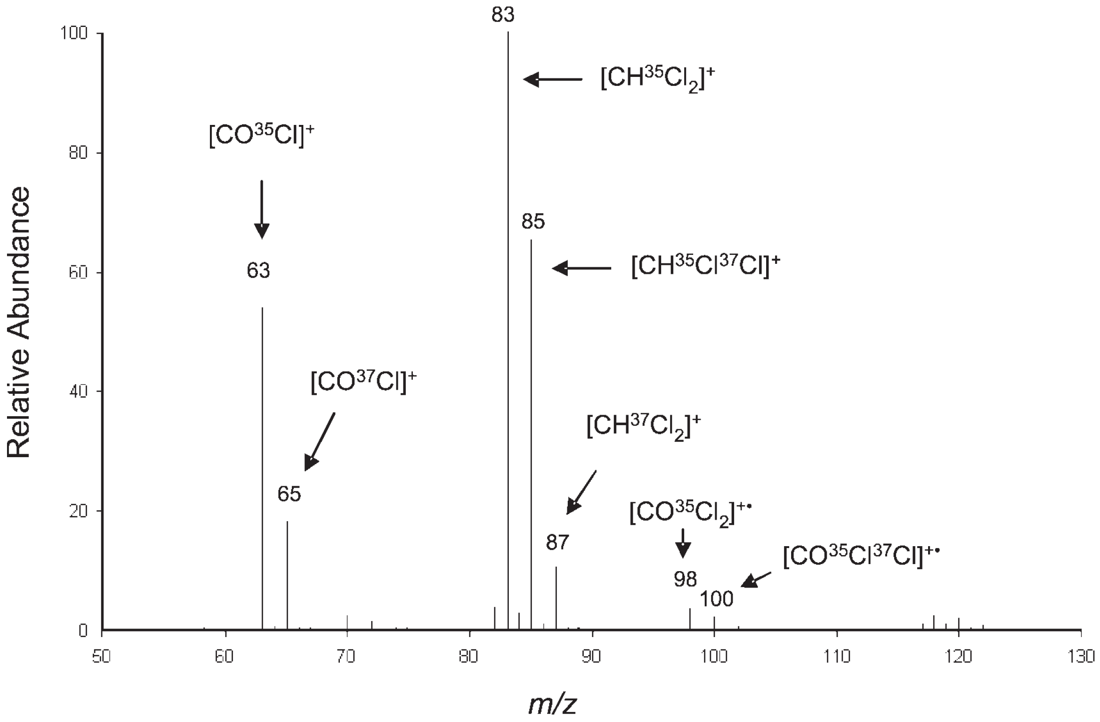

Figure 3. Total mass spectrum for the reaction between $CHCl_3$ and NaClO in a reaction time of 3 minutes. Note the presence of the fragments of *m/z* 63/65 ($[COCl]^+$) and *m/z* 98/100 ($[COCl_2]^{+\bullet}$) indicating the formation of phosgene in such reaction conditions.

Table 1. Comparison between the theoretical and experimental relative intensities of the isotopomeric EI fragments of *m/z* 98/ 100 ($[COCl_2]^{+\bullet}$) and 63/ 65 ($[COCl]^+$)

m/z	Relative Intensity (theoretical)	Relative Intensity (observed)
63	1	1
65	0.325	0.33
98	1	1
100	0.653	0.66

EI fragment ion of *m/z* 63 (the most intense fragment ion in the mass spectrum of phosgene and conveniently absent in the chloroform mass spectrum)[34] increases, concomitantly with the chloroform signal (*m/z* 83) drop, and reaches a maximum intensity after a reaction time of *ca.* 3 minutes. Subsequently, this signal starts to fall and reaches a minimum intensity in *ca.* 7 minutes. These findings indicate that this transient specie, suggested to be phosgene, is formed simultaneously to chloroform consumption and is degraded afterward. In addition, it must be explained that since sodium hypochloride (as well as any basic aqueous solutions) adsorbs CO_2 from air, the monitoring of the EI fragment ion of *m/z* 44, indicative of a possible CO_2 formation in this reaction process, could not be carried out.

Scheme 1 shows a reactional sequence proposed for the chloroform degradation promoted by hypochloride in aqueous acidic medium. It is suggested that the initial step in this process involves the formation of the transient and unstable specie $HOCCl_3$ (trichloromethanol) which was, likely owing to its relatively high polarity and instability, not detected by the mass spectrometer. Finally, from this initial specie, phosgene ($COCl_2$), ClCOOH (chloroformic acid), and finally CO_2, could be consecutively produced by successive additions of H_2O and losses of HCl molecules.

It is astonishing that the suggested reaction sequence displayed in Scheme 1 is similar to that proposed some years ago based on the aerobic enzymatic degradation of chloroform.[35,36] In these papers, the authors suggested that the C-H bond of $CHCl_3$ was oxidized to produce trichloromethanol, ($HOCCl_3$) which was spontaneously converted to phosgene. Phosgene was detected as a stable

$$CHCl_3 + HOCl \xrightarrow{-\,HCl} HOCCl_3 \xrightarrow{-\,HCl} COCCl_2 \xrightarrow[H_2O]{-\,HCl} ClCOOH \longrightarrow CO_2 / H_2O$$

Scheme 1.

adduct with cysteine, namely 2-oxothiazolidine-4-carboxylic acid.

The formation of the unstable intermediate $HOCCl_3$ (trichloromethanol) is suggested to occur via the pathways outlined in Scheme 2. Note that the initial step in this sequence involves a simple and well-known[37] homolytic cleavage of the O-Cl bond in hypochlorous acid (HOCl) to produce HO• and Cl• radicals.

$$HOCl \longrightarrow HO\bullet + Cl\bullet$$

$$Cl\bullet + H_2O \longrightarrow HO\bullet + HCl$$

$$CHCl_3 \xrightarrow{HO\bullet} CCl_3\bullet + H_2O$$

$$CCl_3\bullet + H_2O \longrightarrow HOCCl_3 + H\bullet$$

$$HO\bullet + H\bullet \longrightarrow H_2O$$

Scheme 2.

Note also that only in acidic medium a considerable concentration of this precursor (HOCl) could be formed which, as a consequence, could efficiently promote the chloroform decomposition, as verified in the experiments described herein.

Conclusions

MIMS technique was used to observe the decomposition of chloroform in aqueous acidic medium by sodium hypochloride. Its ability to perform simultaneous monitoring allowed us to identify several reaction intermediates and, consequently, to propose a reaction sequence until the complete degradation of chloroform to CO_2. This work is an additional example of the great efficiency, sensibility and simplicity of the MIMS technique, which might be thoroughly applied in other relevant environmental applications, such as the monitoring of the degradation of other volatile pollutants in aqueous medium.

Acknowledgements

The authors thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG) for financial support. We also thank the referees for their valuable suggestion.

References

1. Johnson, R. C.; Cooks, R. G.; Allen, T. M.; Cisper, M. E.; Hemberger, P. H.; *Mass Spectrom. Rev.* **2000**, *19*, 1.
2. Moraes, L. A. B.; Eberlin, M. N.; Cagnon, J. R.; Urbano, L. H.; *Analyst* **2000**, *125*, 1529.
3. Sharara, K.; Mansouri, J.; Fane, A. G.; Crisp, P. T.; Calderon, P.; Guilhaus, M.; *Water Sci. Technol.* **2000**, *41*, 373.
4. Lauritsen, F. R.; Mendes, M. A.; Aggerholm, T.; *Analyst* **2000**, *125*, 211.
5. Lauritsen, F. R.; Rose, J.; *Analyst* **2000**, *125*, 1577.
6. Mendes, M. A.; Eberlin, M. N.; *Analyst* **2000**, *125*, 21.
7. Riter, L. S.; Takats, Z.; Cooks, R. G.; *Analyst* **2001**, *126*, 1980.
8. Riter, L. S.; Takats, Z.; Charles, L.; Cooks, R. G.; *Rapid Commun. Mass Spectrom.* **2001**, *15*, 1520.
9. Alberici, R. M.; Sparrapan, R.; Jardim, W. F.; Eberlin, M. N.; *Environ. Sci. Technol.* **2001**, *35*, 2084.
10. Alberici, R. M.; Zampronio, C. G.; Poppi, R. J.; Eberlin, M. N.; *Analyst* **2002**, *127*, 230.
11. Mendes, M. A.; Sparrapan, R.; Eberlin, M. N.; *Anal. Chem.* **2000**, *72*, 2166.
12. Allen, T. M.; Falconer, T. M.; Cisper, M. E.; Borgerding, A. J.; Wilkerson, C. W., Jr.; *Anal. Chem.* **2001**, *73*, 4830.
13. Kostiainen, R.; Kotiaho, T.; Mattila, I.; Mansikka, T.; Ojala, M.; Ketola, R. A.; *Anal. Chem.* **1998**, *70*, 3028.
14. Silva, A. C. B.; Augusti, R.; Dalmazio, I.; Windmoller, D.; Lago, R. M.; *Phys. Chem. Chem. Phys.* **1999**, *1*, 2501.
15. Kotiaho, T.; Lauritsen, F. R.; Choudhury, T. K.; Cooks, R. G.; Tsao, G. T.; *Anal. Chem.* **1991**, *63*, 875A.
16. Augusti, R.; Turowski, M.; Cooks, R. G.; *Analyst* **2003**, *128*, 61.
17. Burgos, A. E.; Sinisterra, R. D.; Augusti, R.; Lago, R. M.; *J. Incl. Phenom. Macro.* **2003**, *45*, 149.
18. Lago, R. M.; Silva, A. C. B.; Teixeira, A. C. M.; Augusti, R.; *Analyst* **2003**, *128*, 884.
19. Kotiaho, T.; Hayward, M. J.; Cooks, R. G.; *Anal. Chem.* **1991**, *63*, 1794.
20. Shang, C.; Blatchley, E. R.; *Environ. Sci. Technol.* **1999**, *33*, 2218.
21. Shang, C.; Blatchley, E. R.; *Water Res.* **2000**, *35*, 244.
22. Rios, R. V. R. A.; Da Rocha, L. L.; Vieira, T. G.; Lago, R. M.; Augusti, R.; *J. Mass Spectrom.* **2000**, *35*, 618.
23. Augusti, R.; Dias, A. O.; Rocha, L. L.; Lago, R. M.; *J. Phys. Chem. A* **1998**, *102*, 10723.
24. Wong, P. S. H.; Srinivasan, N.; Kasthurikrishnan, N.; Cooks, R. G.; Pincock, J. A.; Grossert, J. S.; *J. Org. Chem.* **1996**, *61*, 6627.
25. Johnson, R. C.; Koch, K.; Cooks, R. G.; *Ind. Eng. Chem. Res.* **1999**, *38*, 343.
26. Lago, R. M.; Nagem, N. F.; Dalmázio, I.; Augusti, R.; *Rapid Commun. Mass Spectrom.* **2003**, *17*, 1507.

27. Wallace, L. A.; *Crit. Rev. Environ. Sci. Technol.* **1997**, *27*, 113.
28. Mak, F. T.; Cooper, W. J.; Kurucz, C. N.; Nickelsen, M. G.; Waite, T. D. In *Disinfection By-Products in Water Treatment*; Minear; R. A.; Amy, G. L. L., eds., Lewis: Boca Raton, FLA, 1996; p. 131-150.
29. Lubicki, P.; Cross, J. D.; Jayaram, S.; *Decomposition of Chloroform and Trichloroethylene in Deionized Water with the Use of Low Voltage Electron Beam - International Conference on Conduction and Breakdown in Dielectric Liquids*; 12th ed.; Institute of Electrical and Electronic Engineers: Rome, Italy, 1996; p. 442-445.
30. Martin, C. A.; Baltanas, M. A.; Cassano, A. E.; *Environ. Sci. Technol.* **1996**, *30*, 2355.
31. Choi, W.; Hoffmann, M. R.; *Environ. Sci. Technol.* **1997**, *31*, 89.
32. Egli, C.; Stromeyer, S.; Cook, A. M.; Leisinger, T.; *FEMS Microbiology Letters* **1990**, *68*, 207.
33. Mendes, M. A.; Pimpim, R. S.; Koiaho, T.; Barone, J. S.; Eberlin, M. N.; *Quim. Nova* **1996**, *19*, 480.
34. Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. In *The NIST Chemistry WebBook*; Linstrom, P. J.; Mallard, W. G., eds.; National Institute of Standards and Technology (http://webbook.nist.gov): Gaithersburg, MD, 2001.
35. Pohl, L. R.; Bhooshan, B.; Whittaker, N. F.; Krishna, G.; *Biochem. Biophys. Res. Commun.* **1977**, *79*, 684.
36. Mansuy, D.; Beaune, P.; Cresteil, T.; Lange, M.; Leroux, J. P.; *Biochem. Biophys. Res. Commun.* **1977**, *79*, 513.
37. March, J.; *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992, p. 1495.

Received: December 4, 2003
Published on the web: February 4, 2005