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Michel Heninger, Essyllt Louarn, Helene Mestdagh, Joel Lemaire, Stephane Pasquiers, et al.. Real time analysis of toluene degradation in a dielectric barrier discharge plasma. 68th ASMS Conference on Mass Spectrometry and Allied Topics, May 2020, Houston, United States. hal-03331350

HAL Id: hal-03331350

<https://hal.science/hal-03331350>

Submitted on 1 Sep 2021

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Real time analysis of toluene degradation in a dielectric barrier discharge plasma.

Michel Heninger¹, Essyllt Louarn¹, Helene Mestdagh¹, Joel Lemaire¹, Stephane Pasquiers², Nicole Blin Simiand²
¹ ICP, UMR8000, CNRS-Université Paris Sud, Orsay, France
² 2 LPGP, UMR8578, CNRS-Université Paris Sud, Orsay, France

Introduction

Non thermal plasmas can be used to remove pollutants from air. Among other depollution methods it has the advantage of being efficient over a very wide range of concentrations including diluted mixtures (<1000 ppm). However some of the degradation products can be dangerous (even more than the initial species) and care must be taken that the degradation is sufficiently complete.

We here present a study of the degradation of toluene, a reference molecule as it is one of the major aromatic pollutants produced as well indoor by the use of domestic products as outdoor by vehicles exhaust emission.

We have identified and quantified the different products present after plasma treatment of a flow of air containing toluene

Compact FTICR/MS

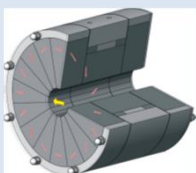
BTrap mass spectrometer (from the AlyXan company) has the following characteristics:

- Use of a permanent magnet → Compact and transportable
- Ion trap: controlled conditions → in-cell chemical reactions.
- Electronic ionization & Chemical ionization (neg or pos) → multiple precursors switch
- High resolution → Molecular formula identification
- Broadband analysis
- Range: few ppb %



Magnetic field

The magnetic field is produced by a structured magnet made with NdFeB segments. It is composed of three Halbach cylinders each divided in 16 segments. The nominal field is 1.5 T and the homogeneity better than 0.5% in the ICR cell volume.



Cell

The cell is cubic (3 cm x 3 cm x 3 cm) with an open configuration geometry to ensure a good pumping of the gas pulses. The two electrodes perpendicular to the bore axis, normally used for excitation are suppressed. The excitation and detection are performed on the same electrodes.



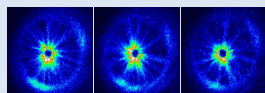
Chemical Ionization

H₃O⁺ ions are first produced by electron ionization on a pulse of H₂O. Then a pulse of the gas present at the reactor output is introduced and the various volatile organic compounds present are ionized by proton transfer reactions.

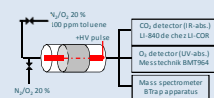
DBD discharge



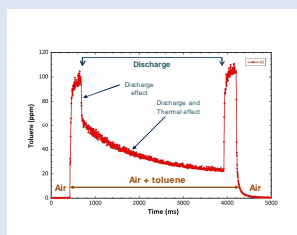
The dielectric barrier discharge reactor is cylindrical. The dielectric is an alumina tube (id 20mm, thickness 3mm). The inner electrode is a stainless steel threaded rod (2mm diameter) and the grounded external electrode is the copper foil (5cm length) seen on the picture.



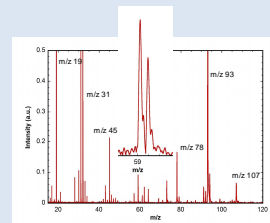
View of the filamentary DBD discharge. This type of discharge is quite efficient for depollution purposes and gets even more efficient at low pollutant concentrations. It can be combined with catalysts to help in achieving complete removal.



A flow of dry air containing various concentrations of toluene in the range 10-100 ppm was prepared by dilution of 100 ppm toluene with air (or eventually N₂). At the exit of the discharge CO₂ and O₃ were measured with specific detectors while the various COV present were followed using the compact FTICR mass spectrometer.

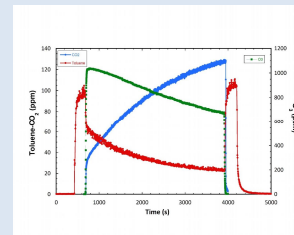
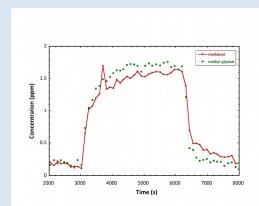


The concentration of toluene, as measured by the FTICR-MS, here initially prepared at 100 ppm shows a rapid fall off when the discharge is turned on. Then the degradation efficiency increases slowly with time, in relation with the self warming of the discharge.



Overall view of the different products formed on a mass spectrum obtained after toluene degradation by the discharge. m/z 19 is the ionic precursor H₃O⁺ and the other peaks correspond to the various species present, after protonation by H₃O⁺.

The zoom at m/z 59 shows that a doublet is present, each of two peaks corresponding to a different compound. They can be attributed to glyoxal and acetone (or propanal as isomers can not be distinguished).



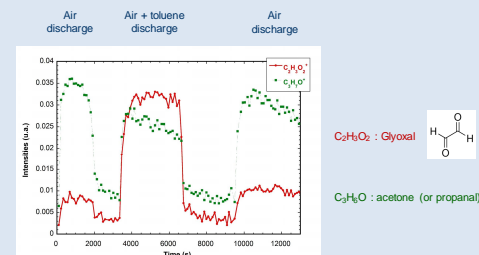
Here the time evolution of the toluene concentration is shown together with the CO₂ and O₃ concentrations as measured using specific detectors. Production of CO₂ increases with time (in relation with a better degradation efficiency) while O₃ decreases.

Experimental mass	Theoretical mass	Delta masses	Molecular formula	Attribution
38.034	38.034	-0.3	H ₂ O	Acetone
39.036	39.036	-2	H ₂ O	Water
31.034	31.033	1.6	H ₂ O ⁺	Water
28.038	28.038	0	CH ₂ N	Hydrogen cyanide
31.038	31.038	0.3	CH ₂ N	Formaldehyde
33.034	33.034	0.6	CH ₂ O	Methanol
42.027	42.024	-0.7	CH ₂ NH	Acetamide
43.038	43.038	0	CH ₂ NH	Acetone
44.034	44.033	0.4	CH ₂ NH	Acetone
45.034	45.034	0.3	CH ₂ NH	Cyano acid, isocyanic acid
47.033	47.033	0.1	CH ₂ NH	Acetaldehyde, Ethanol
47.048	47.048	1.6	CH ₂ NH	Formic acid
48.039	48.039	0.7	CH ₂ NH	Formic acid
57.033	57.034	-0.7	CH ₂ NH	Acetic acid
57.048	57.048	-1.7	CH ₂ NH	Isobutene...
59.030	59.031	-3.3	CH ₂ NH	Glyoxal
59.045	59.049	-0.8	CH ₂ NH	Acetic Propanal
63.029	63.028	0.7	CH ₂ NH	Acetic acid...
62.025	62.024	1.3	CH ₂ NH	Methyl nitrite, Methylene nitrite
64.034	64.033	1.5	CH ₂ NH	Nitric acid
69.038	69.038	0.1	CH ₂ NH	Cyclopentene, isoprene...
73.022	73.028	-0.2	CH ₂ NH	Methyl glyoxal, 2-Propanone, acetic...
76.030	76.030	0.9	CH ₂ NH	Methyl nitrite
79.034	79.034	0.5	CH ₂ NH	Benzene
93.048	93.048	-1.8	CH ₂ NH	Toluene
94.033	94.033	-0.9	CH ₂ NH	Toluene
99.039	99.039	0	CH ₂ NH	?
100.030	100.030	0.2	CH ₂ NH	?
107.033	107.040	-3.7	CH ₂ NH	Benzaldehyde

The molecular formula of the different peaks present on the mass spectrum are attributed using the exact mass corresponding to the peaks.

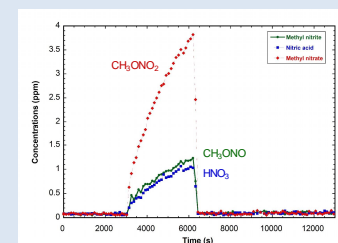
Here the time evolution is shown for two products, methanol (observed at m/z 33) and methyl glyoxal (observed at m/z 73). They are quite close for the two products, with a small increase at the beginning and then staying relatively constant when reaching a plateau.

The trail at the end (when the discharge has been turned off) is probably due to products deposited in the lines.



C₂H₂O₂ : Glyoxal
 C₃H₆O : acetone (or propanal)

As glyoxal and acetone (or propanal) are separated at m/z 59 their specific time evolution can be followed. Propanal (or acetone) is always produced when turning on the discharge even if pure air is flown in the reactor, probably because of species deposited on surfaces. The time evolution for glyoxal is different and shows that it is mainly produced when the discharge is operated on air containing toluene and can be flagged as a toluene degradation product.



To produce m/z 62, m/z 64 and m/z 78 species, nitrogen oxides, N₂O₂, NO₂, NO, are produced in the plasma. The time evolution of the three protonated products shows an increase in concentration with time when the discharge is on. They are more and more abundant when the temperature in the discharge increases by self warming.

Conclusion

With the compact FTICR mass spectrometer (BTrap from the AlyXan company) we can identify the degradation products formed in the discharge and also follow their time evolution, which is essential to understand the reactivity occurring in the discharge.

The picture given by the mass spectrometer is completed by measurement with specific detectors for species that are not detected by chemical ionization. Our results can also be compared with measurements made by gas chromatography and FTIR (not presented here). The time resolved measurements clearly show a thermal effect leading to a better degradation when the discharge gets warmer.

The real time analysis of all the different byproducts will help in modelling all the reaction mechanisms underway during the discharge.