Decomposition of mixtures of organic compounds in atmospheric plasma

E. Marotta[*], M. Schiorlin, E. Gazza, C. Paradisi

Department of Chemical Sciences, Università di Padova, via Marzolo 1, 35131 Padova, Italy
[(*)] ester.marotta@unipd.it

The decomposition mechanisms of methanol, *n*-hexane and tetrachloromethane treated as binary mixtures in air were studied in a wire-cylinder corona reactor energized by positive and negative DC. Competition and entrainment effects between the different organic compounds were evidenced and rationalized on the basis of the chemical characteristics and reactivities of the molecules under investigation.

The application of atmospheric plasma-based technologies to the decomposition of organic compounds in air and water is rapidly growing and under continuous development. Atmospheric plasmas are very conveniently produced by corona or dielectric barrier discharges in air at room temperature and atmospheric pressure and can be used to induce the exhaustive oxidation of the organic pollutants to CO_2. To optimize the efficiency and the product selectivity of these processes, it is important to study and understand the complex reactions of the organic compounds within these plasmas. The majority of studies so far have involved simplified models of air and water containing a single organic pollutant [1,2]. From such investigations it was recognized that, besides the effects due to the specific experimental apparatus and to the type and polarity of the voltage applied to produce the discharge, there is also generally a dependence of the process efficiency on the chemical nature of the organic compound used and on its initial concentration [1-4]. In a step towards more realistic models, we have recently undertaken the investigation of binary mixtures of two different organic pollutants to identify possible competition and entrainment effects in the treatment both of air and water using two different experimental systems. In this report, the experiments and the results obtained in the treatment of air will be presented.

Air purification from Volatile Organic Compounds (VOCs) is performed with a wire-cylinder corona reactor, in which electrical discharges are produced by the application of a negative or positive DC voltage [3]. Common chemical diagnostics includes on-line analysis with FT-IR and GC coupled with different detectors (TCD, MSD, FID). Optical Emission Spectroscopy was also recently applied for the detection of excited species. Additional studies dealing with the ion chemistry of the organic compounds in air plasma are conducted with an APCI (Atmospheric Pressure Chemical Ionization) mass spectrometer and allow to identify major ions present in the plasma and the ion-molecule reactions responsible for their formation [5]. For the present investigation, three important VOCs of widely different chemical nature and properties were selected, namely methanol (CH_3OH), *n*-hexane ($n\text{-}C_6H_{14}$) and tetrachloromethane (CCl_4). Preliminary experiments were performed to characterize the behaviour of each individual VOC, specifically with regard to the effect of the VOC initial concentration. Subsequently the behavior of the three binary mixtures ($CH_3OH + n\text{-}C_6H_{14}$; $CH_3OH + CCl_4$; $n\text{-}C_6H_{14} + CCl_4$) was examined. The efficiency of VOC removal is expressed by the energy constant k_E, which is derived by interpolation of the residual VOC concentration, *[VOC]*, as a function of the specific input energy (*SIE*), i.e. the energy per unit volume ($kJ·L^{-1}$), with equation (1)

$$[VOC] = [VOC]_0 \cdot e^{-k_E \cdot SIE} \tag{1}$$

where *[VOC]$_0$* is the initial VOC concentration [2,6].

The energy constants obtained in the treatment of methanol, *n*-hexane and tetrachloromethane, alone and in mixture, with negative DC corona (−DC) are reported in Table 1.

The order of reactivity when the three organic compounds are treated separately with −DC is *n*-C_6H_{14} > CH_3OH > CCl_4. This order reflects the reactivity of the organic molecules with O atoms and OH radicals, which were previously recognized as the main reactive species responsible for the initiation of the VOCs decomposition with −DC [7]. It is also found that, for each VOC, k_E decreases with increasing VOC initial concentration (Table 1). This is a well known phenomenon due to the competition for the reactive species by oxidation intermediates formed from the original VOC [8]. Considering now binary VOC mixtures, if one assumes that the two different VOCs react with the

same reactive species and that they do not interact one with the other in any specific way, then a decrease of the k_E obtained when each VOC is treated alone at the same concentration is expected. This is due to the competition for the reactive species.

The results reported in Table 1, however, show that the situation is more complex as the result of specific chemical reactions. Thus, it was observed that in many cases the treatment in mixture does not entail a significant change of k_E with respect to that obtained when the VOC is treated alone at the same initial concentration. This is for example the case of *n*-hexane treated in mixture with methanol but also with tetrachloromethane (Table 1). This could

Table 1. Energy constants obtained in the treatment of CH_3OH, *n*-C_6H_{14} and CCl_4, alone and in mixture, with –DC.

VOCs and concentration in air	k_E (CH_3OH)	k_E (*n*-C_6H_{14})	k_E (CCl_4)
CH_3OH 250 ppm	1.0	-	-
CH_3OH 500 ppm	0.85	-	-
n-C_6H_{14} 250 ppm	-	1.7	-
n-C_6H_{14} 500 ppm	-	0.95	-
CCl_4 250 ppm	-	-	0.13
CCl_4 500 ppm	-	-	0.12
CH_3OH 250 ppm + *n*-C_6H_{14} 250 ppm	-[a]	1.6	-
CH_3OH 250 ppm + CCl_4 250 ppm	1.95	-	0.13
n-C_6H_{14} 250 ppm + CCl_4 250 ppm	-	1.8	0.095

[a] the trend of methanol in this mixture does not fit an exponential decay

indicate that the oxidation of the two compounds is initiated by different mechanisms and/or reactive species, thus the two VOCs are not much influenced one by the another. The fact that tetrachloromethane also is not influenced by the presence of *n*-hexane confirms this hypothesis (Fig. 1a). On the contrary, methanol shows an anomalous behavior (Fig. 1b), as the lowest energy value applied determines a significant decomposition degree, but for higher energy values the decomposition efficiency decreases; the trend is exponential from the second experimental point on. We attribute the change in efficiency observed at higher energies to the competition for the reactive species exerted by all the intermediate products formed from *n*-hexane. This is the only
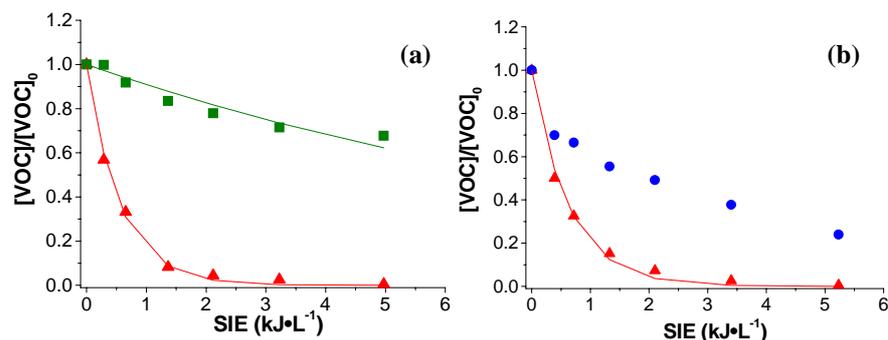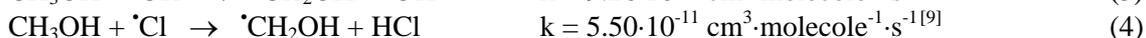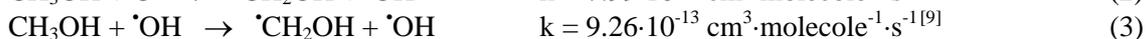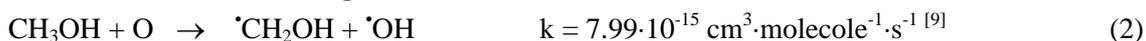

Fig. 1: Decomposition efficiency of a mixture of (a) *n*-hexane (▲) and tetrachloromethane (■) (250 ppm each) and (b) *n*-hexane (▲) and methanol (●).

compound among the three under investigation which has more than one atom of carbon and which consequently produces many different intermediates [6]. In contrast, methanol, which is intrinsecally less reactive than *n*-hexane, does not succeed to compete with *n*-hexane and its intermediates.

Particularly interesting is the case of methanol treated in mixture with tetrachloromethane as its decomposition efficiency almost doubles with respect to that obtained when treated alone at the same initial concentration and becomes 2.3 times larger than found when treated alone at an initial concentration of 500 ppm. This increase can be ascribed to the reaction of methanol with atomic chlorine formed from CCl_4, as the kinetic constant of this reaction is far higher than those of the reactions with O and $^\bullet OH$, as reported below:

$CH_3OH + O \rightarrow {}^\bullet CH_2OH + {}^\bullet OH$ $\qquad$ k = $7.99 \cdot 10^{-15}$ $cm^3 \cdot molecole^{-1} \cdot s^{-1}$ [9] $\qquad$ (2)

$CH_3OH + {}^\bullet OH \rightarrow {}^\bullet CH_2OH + {}^\bullet OH$ $\qquad$ k = $9.26 \cdot 10^{-13}$ $cm^3 \cdot molecole^{-1} \cdot s^{-1}$ [9] $\qquad$ (3)

$CH_3OH + {}^\bullet Cl \rightarrow {}^\bullet CH_2OH + HCl$ $\qquad$ k = $5.50 \cdot 10^{-11}$ $cm^3 \cdot molecole^{-1} \cdot s^{-1}$ [9] $\qquad$ (4)

Contrary to the reactions with neutral species, the negative ion chemistry of the VOCs under consideration does not seem to have an active role in the decomposition of the organic compounds with –DC. From the APCI-MS experiments it can be observed that *n*-hexane does not form negative ions [7], methanol complexes the ions coming form air, which are mainly $O_2^{-\bullet}$ and $O_3^{-\bullet}$, and

tetrachloromethane produces Cl^- by reaction with $O_2^{-\bullet}$ [10]. When analyzed in binary mixtures, the presence of n-hexane is completely invisible in the spectra both with CH_3OH and CCl_4; in the spectra of the mixture of CH_3OH and CCl_4, Cl^- is complexed by molecules of methanol, while no ion-molecule reactions are observed supporting the hypothesis that no ionic processes are responsible for the increase in efficiency observed in the $-DC$ corona processing of methanol mixed to tetrachloromethane.

When the same organic compounds are treated with $+DC$, significant differences are observed in their behavior. The energy constants obtained are reported in Table 2. As it can be observed, the order of reactivity of the single compounds is different from that obtained with $-DC$, i.e $CH_3OH > n$-$C_6H_{14} > CCl_4$. In a previous study dealing with n-hexane, it was found that the crucial initiation steps in the decomposition of this compound with $+DC$ are mainly ionic

Table 2. Energy constants obtained in the treatment of CH_3OH, n-C_6H_{14} and CCl_4, alone and in mixture, with $+DC$.

VOCs and concentration in air	k_E (CH_3OH)	k_E (n-C_6H_{14})	k_E (CCl_4)
CH_3OH 250 ppm	0.46	-	-
CH_3OH 500 ppm	0.29	-	-
n-C_6H_{14} 250 ppm	-	0.33	-
n-C_6H_{14} 500 ppm	-	0.19	-
CCl_4 250 ppm	-	-	0.071
CCl_4 500 ppm	-	-	0.069
CH_3OH 250 ppm + n-C_6H_{14} 250 ppm	$-^a$	0.275	-
CH_3OH 250 ppm + CCl_4 250 ppm	0.65	-	0.087
n-C_6H_{14} 250 ppm + CCl_4 250 ppm	-	0.44	0.095

^{a} the trend of methanol in this mixture does not fit an exponential decay

reactions with the species $O_2^{+\bullet}$ and H_3O^+. Because also for methanol the ion-molecule reactions with $O_2^{+\bullet}$ and H_3O^+ are faster than its reactions with the oxidizing neutral species (molecules, atoms and radicals) present in the system, we can hypothesize that also methanol is attacked more efficiently by ions than by neutrals. Thus, the study of the positive ion chemistry of these compounds in atmospheric plasma becomes very important. As found earlier [7,11], n-hexane forms mainly the species $C_6H_{13}^+$ and some lower alkyl cations; CH_3OH is prevalently protonated and at higher energy fragments to CH_3^+; CCl_4 forms mostly CCl_3^+, which can be complexed by water molecules [10]. When studied in mixture, it was observed that methanol exerts with n-hexane the same role as water, that is it complexes the ions coming from n-hexane and in particular the most abundant species, $C_6H_{13}^+$. In the case of the mixture of n-hexane with water, the complexation phenomenona entail a decrease in the decomposition efficiency of n-hexane with $+DC$ [6,7]. Interestingly, the same effect is observed when n-hexane is treated in mixture with methanol as its energy constant decreases by 20% (Table 2). The efficiency reduction can be attributed to the fact that complexed ions are less reactive than the bare species. On the other hand, methanol shows again, as in $-DC$, a decrease in reactivity after the exponential point taken at the lowest energy value. We think that this also can be due to the efficient competition by the numerous intermediate products formed from n-hexane [6].

On the contrary, when methanol and tetrachloromethane are present together in the air plasma generated by $+DC$, new positive ions produced by ion-molecule reactions between them are observed. The APCI-MS spectra obtained with two different molar ratios of the two VOCs and with deuterated methanol instead of CH_3OH are shown in Fig. 2.

Fig. 2: APCI-MS spectra in positive ion mode of a mixture of CH_3OH and CCl_4 (a) 1:1 and (b) a 1:20 and of (c) a 1:1 mixture of CH_3OH and CCl_4.

As reported in the figure, the structure of the new ionic species formed in the mixture of methanol and tetracloromethane is due to the partial or complete replacement of chlorine atoms by methoxy
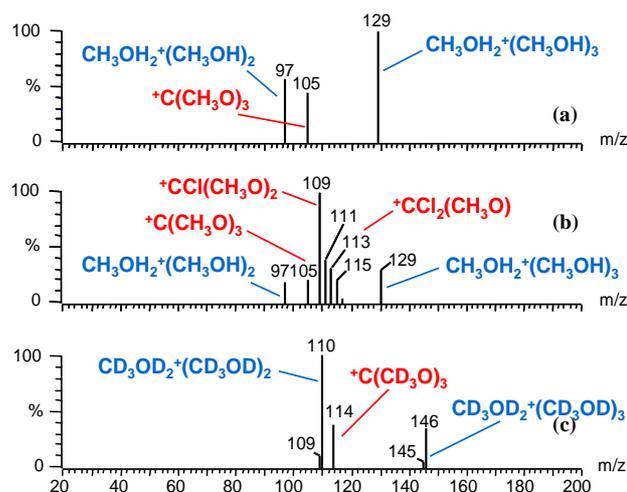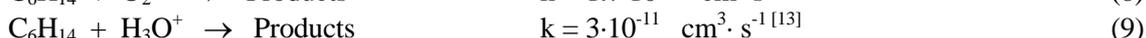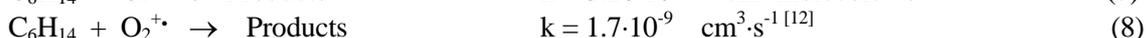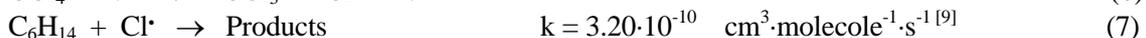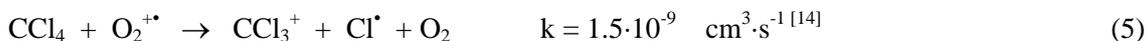
groups. Based on previous studies on similar systems, we can safely ascribe their formation to the reaction of protonated methanol with tetrachloromethane followed by the loss of two HCl molecules and subsequent steps of methanol addition and HCl elimination, as reported in Scheme 1. This reaction could contribute to the increase in the decomposition efficiency of methanol and tetrachloromethane when they are treated in mixture (Table 2).
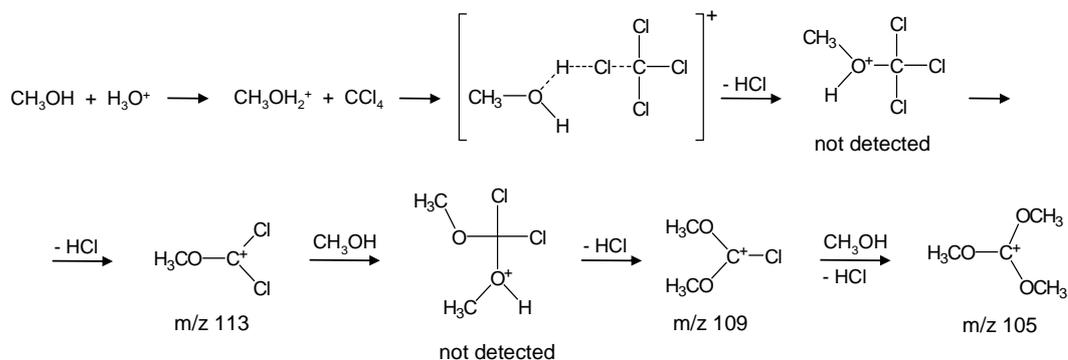
Scheme 1

When n-hexane is mixed with CCl_4, the same ions are observed as found in the spectra of the single compounds, with no products due to ion-molecule reactions. Thus the increase in efficiency observed for both compounds must be due to a different process. We must consider that, whatever is the decomposition mechanism of CCl_4, as for example mainly due to reaction with $O_2^{+\bullet}$ (eq. 5) or to electron induced dissociation (eq. 6), chloro atoms are formed from this compound. Thus, we can attribute the higher reactivity observed for n-hexane treated in mixture with CCl_4 to its reaction with Cl atoms (eq. 7). This is true even if the rate constant for reaction of n-hexane with $Cl^\bullet$ is lower than those with $O_2^{+\bullet}$ and H_3O^+ (eq. 8 and 9) because reaction (7) represents an additional decomposition pathway for n-hexane which can become quite significant in the presence of a high concentration of $Cl^\bullet$.

$$CCl_4 + O_2^{+\bullet} \rightarrow CCl_3^+ + Cl^\bullet + O_2 \qquad k = 1.5 \cdot 10^{-9} \quad cm^3 \cdot s^{-1} \, [14] \qquad (5)$$
$$CCl_4 + e^- \rightarrow {}^\bullet CCl_3 + Cl^\bullet + e^- \qquad\qquad\qquad\qquad\qquad\qquad (6)$$
$$C_6H_{14} + Cl^\bullet \rightarrow Products \qquad k = 3.20 \cdot 10^{-10} \quad cm^3 \cdot molecole^{-1} \cdot s^{-1} \, [9] \qquad (7)$$
$$C_6H_{14} + O_2^{+\bullet} \rightarrow Products \qquad k = 1.7 \cdot 10^{-9} \quad cm^3 \cdot s^{-1} \, [12] \qquad (8)$$
$$C_6H_{14} + H_3O^+ \rightarrow Products \qquad k = 3 \cdot 10^{-11} \quad cm^3 \cdot s^{-1} \, [13] \qquad (9)$$

In conclusion, the reported results provide evidence for specific chemical interactions between two different VOCs reacting within the same air plasma. Such interactions can affect quite significantly the process efficiency.

References
[1] A. Fridman, *"Plasma Chemistry"*, Cambridge University Press, (2008).
[2] H.-H. Kim, *Plasma Process. Polym.* **1** (2004) 91-110.
[3] E. Marotta, M. Schiorlin, M. Rea, C. Paradisi, *J. Phys. D: Appl. Phys.* **43** (2010) 124011.
[4] M. Schiorlin, E. Marotta, M. Rea, C. Paradisi, *Environ. Sci. Technol.* **43** (2009) 9386-9392.
[5] A. Donò, C. Paradisi, G. Scorrano, *Rapid Commun. Mass Spectrom.* **11** (1997) 1687-1694.
[6] E. Marotta, A. Callea, M. Rea, C. Paradisi, *Env. Sci. Technol.* **41** (2007), 5862-5868.
[7] E. Marotta, A. Callea, X. Ren, M. Rea, C. Paradisi, *Plasma Process. Polym.* **5** (2008) 146-154.
[8] R. Rudolph, K.-P. Francke, H. Miessner, *Plasma Chem. Plasma Process.* **22** (2002) 401-412.
[9] Lias, S. G. Ionization Energy Evaluation. In *NIST Chemistry-WebBook, NIST Standard Reference Database No. 69*; Maillard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD; 2006; http://webbook.nist.gov/chemistry/.
[10] E. Marotta, G. Scorrano, C. Paradisi, *Plasma Proc. Polym.* **3** (2005), 209-217.
[11] E. Marotta, C. Paradisi, *J. Am. Soc. Mass Spectrom.* **20** (2009), 697-707.
[12] P. Spanel, D. Smith, *Int. J. Mass Spectrom.* **181** (1998) 1-10.
[13] S. T. Arnold, A. A. Viggiano, R. A. Morris, *J. Phys. Chem. A* **101** (1997) 9351-9358.
[14] P. Spanel, D. Smith, *Int. J. Mass Spectrom.* **184** (1999) 175-181.