#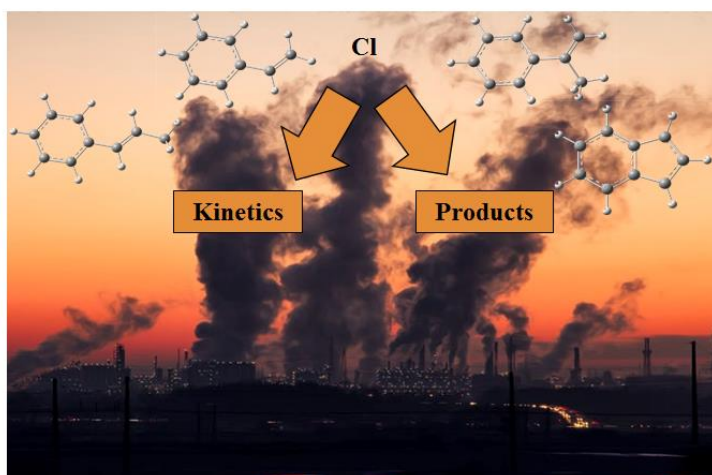 Atmospheric sink of styrene, α-methylstyrene, trans-β-methylstyrene and indene: Rate constants and mechanisms of the Cl atoms initiated degradation

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## Abstract

The kinetics and products of the oxidation of four aromatic compounds such as styrene, α-methylstyrene, trans-β-methylstyrene and indene with Cl atoms were determined at atmospheric pressure and room temperature. Kinetics experiments were carried out in a 400 L Teflon reaction chamber using GC-FID for the analysis and products were determined using a 56 L quartz-glass reactor coupled to FTIR spectrophotometer. The rate constants at 298 K, using different reference compounds, were (in units of $cm^3$ $molecule^{-1}$ $s^{-1}$): $k_{styrene} = (1.29\pm0.52)\times10^{-10}$, $k_{\alpha\text{-methylstyrene}} = (1.55\pm0.27)\times10^{-10}$, $k_{trans\text{-}\beta\text{-methylstyrene}} = (1.09\pm0.23)\times10^{-10}$ and $k_{indene} = (1.01\pm0.30)\times10^{-10}$. Observations with FTIR suggest that the main reaction is the additions of the Cl to the aliphatic chain of the aromatic molecules. We found benzaldehyde, benzoyl chloride, formaldehyde and formyl chloride from styrene; acetophenone, formaldehyde and formyl chloride from α-methylstyrene; and benzaldehyde, formaldehyde and acetyl chloride from trans-β-methylstyrene, as the main oxidation products. DFT theoretical calculations were

performed in order to shed light on the identification of the reaction products. To the best of our knowledge, this work represents the first determination of the rate coefficients and products for the reaction of the Cl atoms with these compounds, except for the rate constant of styrene which has been study previously. Estimated atmospheric lifetime for these four compounds range from days to a few hours depending on the tropospheric oxidant.

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**Keywords:** Chlorine atoms, styrenes, indene, rate coefficients, mechanisms, DFT calculations.

1. **Introduction**

Styrene, α-methylstyrene (AMS), trans-β-methylstyrene (TBMS) and indene are aromatic compounds that can be emitted into the atmosphere from different sources such as solvents, combustion (i.e., gasoline and diesel engines), building materials, adhesives and industrial processes (Calvert et al., 2002; Okada et al., 2012; Knighton et al., 2012; Zhang et al., 2017). As other aromatic compounds, they are common trace components of the urban atmosphere, are toxic to humans, are considered to be one of the most important secondary organic aerosol (SOA) precursors (Odum et al., 1997; Na et al., 2006; Kroll and Seinfeld, 2008; Hallquist et al., 2009; Freney et al., 2014; Diaz de Mera et al., 2017) and primary contributors to photochemical ozone formation (Derwent, 1996; Na, 2005; Berezina et al., 2017). Thus, considering the wide range of uses and harmful health or potential environmental effects, an evaluation of styrenes and indene atmospheric persistence and of their degradation products is needed. These chemicals can be removal from the atmosphere via reactions with OH radicals during the daytime, $NO_3$ radicals at night, $O_3$ during both day and night, Cl atoms in coastal region or undergo direct photolysis (Finlayson-Pitss and Pitts, 2000). Literature data on the OH reaction with styrene, AMS, TBMS and indene indicate that these processes are quite fast $(6\text{-}8)\text{x}10^{-11}$ $cm^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Aschmann, 1988, Bignozzi, 1981; Kwok et al., 1997). Moreover, if we also take into account that the rate constants for the reactions of Cl with many VOCs is significantly faster than the corresponding reactions of OH by up to several orders of magnitude (Atkinson et al., 2006), then it is expected to their lifetimes are low. Therefore, it is important to evaluate the atmospheric importance of each loss processes, in addition to the photolysis, since strong absorption of about $10^{-18}$ $cm^2$ molecule$^{-1}$ has been observed over the wavelengths range 260–280 nm (Le Person et al., 2008).

Up to our knowledge, this is the first study of AMS, TBMS and indene with Cl. Styrene has been studied previously with Cl (Shi and Bernhard, 1997) and with the other tropospheric oxidants (Atkinson and Aschmann, 1988; Tuazon et al, 1993; Bignozzi, 1981; Cho et al, 2014; Butchta et al., 1993; Le Person et al., 2008; Atkinson et al., 1982; Zhang et al., 1994). For AMS only studies with OH (Bignozzi et al., 1981) and $O_3$ (Le Person, 2008) were found in literature. While studied with OH were reported for
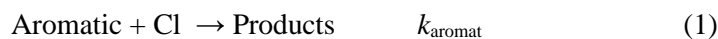
TBMS (Bignozzi et al., 1981) and for indene with OH, $NO_3$ (Kwok et al., 1997) and $O_3$ (Le Person et al., 2008). Even though Cl atom concentrations are lower than the OH radical concentration, Cl atom reactions are significantly important in polluted mid-continental regions in industrial locations, in marine boundary layers and in urban polluted areas (Osthoff, 2008; Thornton et al., 2010), where can compete easily with OH radical. Therefore an investigation of the degradation of these four compounds in the gas phase with Cl atoms were performed in this work, in order to assess any possible environmental consequences.

## 2. Experimental Section

### 2.1.- Kinetic study

A relative kinetic technique was used to determine the rate constants of the reactions of styrene, AMS, TBMS and indene with Cl atoms. A detailed description of the reactor can be found elsewhere (Rodriguez et al., 2015) and only a brief general overall description is given here. Experiments were carried out in a 400 L Teflon bag housed in an isothermal cabinet with six fluorescent lamps (Philips TUV G13, 36W, $\lambda = 254$ nm) mounted on the walls. All experiments were performed at $298 \pm 1$K in ~760 Torr total pressure of Air/$N_2$ diluent. The decay of reactants and reference compounds was monitored by gas chromatography with flame ionization detection, GC-FID (Shimadzu 2010), using a capillary column (size: 30 m × 0.32 mm × 1 μm. Meta.X5 Teknokroma) maintained isothermally at 125ºC. The injection step was repeated 10 to 15 times in each kinetic experiment, and this set of experiments was performed four to six times on different dates, changing the reactant concentrations. The concentration ranges of the reactants were as follows, in molecules $cm^{-3}$: Aromatic compounds $(0.2–1.6) \times 10^{15}$, reference compound $(0.4–5.3) \times 10^{15}$ and $CCl_3COCl$ $(0.7–3.2) \times 10^{15}$. The standard deviation in the measurement of concentrations was obtained by repeated injections of the unreacted mixture within the range of concentration of the kinetic experiments. Studied compounds and reference compounds were determined with a precision of ± 1-3% of their initial concentrations.

In the conducted relative kinetic experiments the following reactions take place:

$$\text{Aromatic} + \text{Cl} \rightarrow \text{Products} \qquad k_{\text{aromat}} \qquad (1)$$

$$\text{Reference} + \text{Cl} \rightarrow \text{Products} \qquad k_{\text{ref}} \qquad (2)$$

where $k_{\text{aromat}}$ and $k_{\text{ref}}$ are the rate coefficients for the studied compounds and the reference hydrocarbon with Cl, respectively.

In smog chamber experiments it is important to check for unwanted loss of reactants and products via photolysis, dark chemistry and heterogeneous reactions; so trichloroacetyl chloride ($CCl_3COCl$) was employed as Cl source since $Cl_2$ reacts with the studied compounds in the dark. The tests also showed

negligible lamp photolysis losses for the reference compounds. However, aromatic compounds had to be taken into account in the kinetic data analysis since they showed photolysis losses,

$$\text{Aromatic} + h\mu \rightarrow \text{Products} \qquad k_{ph} \qquad\qquad (3)$$

Kinetic treatment of reactions 1−3 leads to the following relationship:

$$\ln\left(\frac{[aromatic]_0}{[aromatic]_t}\right) - k_{ph}(t - t_0) = \frac{k_{aromat}}{k_{ref}}\ln\left(\frac{[reference]_0}{[reference]_t}\right)$$

where $k_{aromat}$, $k_{ref}$, and $k_{ph}$ are the rate coefficients for reactions 1−3, respectively, and subscripts 0 and t indicate concentrations at the beginning of the reaction, $t_0$, and at time t, respectively. Thus, a plot of $(\ln[Aromatic]_0/[Aromatic]_t)$- $k_{ph}(t - t_0)$ versus $(\ln[reference]_0/[reference]_t)$ should be a straight line passing through the origin and whose slope yields the ratio of $k_{aromat}/k_{ref}$.

## 2.2.- Mechanistic study

Product experiments were performed using air as bath gas in a 56 L Quartz-glass reactor surrounded by six fluorescent lamps (same as kinetics experiments). A detailed description of the reactor can be found elsewhere (Bravo et al., 2013) and only a brief description is given here. The reactor was coupled to a Bruker VERTEX 80 V Fourier-transform infrared (FTIR) spectrophotometer equipped with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. A white type multiple-reflection mirror system (Saturn Series Multi-Pass cells) set at a total optical path length of 197 m is mounted inside the reactor. This optical system was used for sensitive monitoring of reactants and products in the IR spectral range $4000 – 600 \text{ cm}^{-1}$ and the spectral resolution used in all experiments was $1 \text{ cm}^{-1}$. All the experiments were performed at approximately $298 \pm 1$ K and 760 Torr of NOx-free air. Mixtures of the compound of interest in air were obtained in this way and allowed to stand 30 minutes to allow good mixing. Again, in order to verify aromatic compounds are removed solely by reaction with Cl atoms, various tests similar to kinetic experiments were performed. Photolysis loss of aromatic compounds was confirmed by irradiating with the fluorescent lamps in air and in the absence of the radical precursors. Typically, 64 interferograms were co-added per spectrum over a period of approximately 1 min, and around 10−15 spectra were collected during the course of the experiment. The initial concentrations of the organic compounds (1ppmV $= 2.47 \times 10^{13}$ molecule $\text{cm}^3$ at 298 K and 760 Torr of total pressure) were as follow: aromatic compounds ($5 \times 10^{13}– 1.0 \times 10^{14}$) and $CCl_3COCl$ ($7.4 \times 10^{13}– 2.0 \times 10^{14}$). The reactants were monitored at the following infrared absorption frequencies (in $\text{cm}^{-1}$): 695 and 909.5 for styrene, 702 and 895.2 for AMS, 733.5 and 962 for TBMS and 765.5 for indene.

**2.3 DFT calculations.**

DFT theoretical calculations were conducted in order to shed light on the identification of the reaction products because of the challenge of find commercially available standards for FTIR product experiments or when the nature of the compound avoided carrying out the calibration since it stuck in the reactor ducts. Theoretical calculation were performed using the Gaussian09 (Rev. C.01) set of programs (Frisch et al., 2009). The choice of level of theory and basis set are critical to obtain accurate results. DFT level of theory (B3LYP) were combined with different basic set (6-31G**, 6-311G** and 6-311+G**) and tested over a series of possible degradation products to perform their geometries, and obtain their infrared wavenumber. Molecular structures were first optimized, followed by calculation of vibrational wavenumbers. No symmetry constraints were imposed. In all cases the absence of negative wavenumbers confirmed that we had obtained a minimum on the potential energy surface. When more than one minimum was found, the structure with the lowest Gibbs free energy was used. A root-mean-square deviation analysis were performed over the computed vibrational modes when compare to experimental data for the studied compounds. We found the B3LYP/6-311G** method as the most appropriated to obtain accurate infrared spectra. The wavenumbers of the main calculated vibrational modes can be related to the positions of the important experimental absorption bands and the two quantities plotted against each other (see Supporting Material). A good correlation is found and, thus, the regression fits from these plots was used to obtain rescaled wavenumbers. $\nu_{scal}$ , from the theoretical B3LYP data, $\nu_{calc}$:

$$\nu_{scal} = 0.945\nu_{calc} + 14.39 \text{ cm}^{-1} \qquad r^2 = 0.999 \qquad \text{B3LYP/6-31G**} \qquad (1)$$

**Chemicals**

Reagents were obtained from commercial sources at the following purities: styrene ($\geq$99%, Aldrich), α–methylstyrene (99%, Aldrich), trans-β-methylstyrene (99%, Aldrich), indene (98%, Aldrich), trichloroacetyl chloride (99%, Aldrich), ethane (>99%, Aldrich), propene (>99%, Aldrich), cyclohexane (99.9%, Aldrich), heptane (99%, Aldrich), octane (>99%, Acros Organics), benzaldehyde (>99.5%, Aldrich), acetophenone (>99%, Sigma-Aldrich), acetyl chloride (>99%, Sigma-Aldrich), benzoyl chloride (99%, Sigma-Aldrich), formaldehyde (37% w/w, Sigma-Aldrich). Synthetic air (99.999%, Air Liquide) and $N_2$ (99.999%, Air Liquide) were employed as bath gases for the experiments, and He (99.998%, Air Liquide) was used as GC carrier gas.

## 3. Results and Discussion

### 3.1. Kinetic studies

The rate coefficients for the reactions of the studied aromatic compounds with Cl atoms were

measured using as reference compounds cyclohexane, n-heptane and n-octane, whose rate coefficients are: $k_{Cl+cyclohexane} = (2.91\pm0.31)\times10^{-10}$ (Li and Pirasteh, 2006), $k_{Cl+heptane} = (3.50\pm0.13)\times10^{-10}$ (Anderson et al., 2007), $k_{Cl+octane} = (3.22\pm0.36)\times10^{-10}$ (Li and Pirasteh, 2006). All the $k$ values are in units of $cm^3$ $molecule^{-1}$ $s^{-1}$. Since retention time of indene overlaps with heptane and octane, ethane and propene were used as reference compounds in the kinetic study of this compound, ($k_{Cl+ethane}= (5.85\pm0.55)\times10^{-11}$ (Hitsuda et al., 2001), $k_{Cl+propene}= (2.31\pm0.29)x10^{-10}$ (Stutz et al., 1998). Representative plots of the kinetic data for these reactions are displayed in Figure 1. The rate coefficients obtained in this study, at 298 K in atmospheric pressure of air and $N_2$, after calculating the average values are summarized in Table 1. The errors quoted are a combination of twice the standard deviation arising from the least-squares fit of the straight lines and the corresponding error to the reference rate coefficients. The experiments were performed in $N_2$ and synthetic air to test for potential systematic errors due to secondary reactions and to obtain a better approach to atmospheric conditions. The obtained results were independent of the bath gas used, which suggests that there is no interference from secondary reactions with $O_2$.
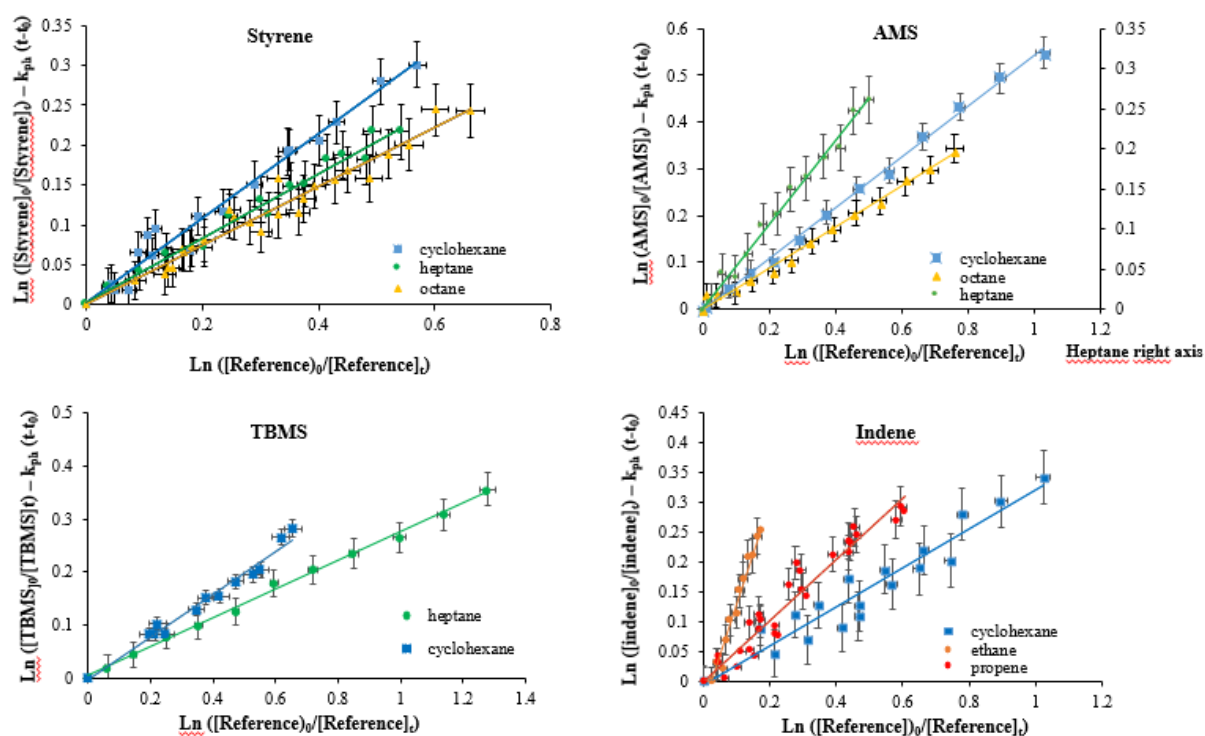


Figure 1.- Kinetic data plots for the reactions of styrene, AMS, TBMS and indene with Cl at 298 ± 1 K and ~ 760 torr of $N_2$ or Air.

**Table 1.** Rate constants ratios for the photolysis process and reaction with Cl together and only by reaction with Cl atoms of studied aromatic compounds-at 298±1 K and atmospheric pressure of $N_2$ or

Air.

| Compound | Reference | $k_{aromat(Cl+ph)}/k_{ref}$ | $k_{Cl+ph}$ $(cm^3\ molecule^{-1}\ s^{-1})$ | $k_{aromat\ (Cl)}/k_{ref}$ | $k_{Cl}$ $(cm^3\ molecule^{-1}\ s^{-1})$ |
|---|---|---|---|---|---|
| Styrene | Cyclohexane | $1.13\pm0.08$ | $(3.28\pm0.59)\times10^{-10}$ | $0.49\pm0.10$ | $(1.43\pm0.61)\times10^{-10}$ |
| | Heptane | $0.86\pm0.06$ | $(3.01\pm0.44)\times10^{-10}$ | $0.36\pm0.03$ | $(1.26\pm0.22)\times10^{-10}$ |
| | Octane | $0.92\pm0.09$ | $(2.96\pm0.68)\times10^{-10}$ | $0.37\pm0.11$ | $(1.19\pm0.72)\times10^{-10}$ |
| | | | $\mathbf{(3.08\pm0.57)\times10^{-10}}$ | | $\mathbf{(1.29\pm0.52)\times10^{-10}}$ |
| AMS | Cyclohexane | $0.62\pm0.04$ | $(1.80\pm0.31)\times10^{-10}$ | $0.50\pm0.04$ | $(1.46\pm0.28)\times10^{-10}$ |
| | Heptane | $0.65\pm0.04$ | $(2.28\pm0.30)\times10^{-10}$ | $0.49\pm0.04$ | $(1.72\pm0.29)\times10^{-10}$ |
| | Octane | $0.57\pm0.02$ | $(1.83\pm0.25)\times10^{-10}$ | $0.46\pm0.03$ | $(1.48\pm0.25)\times10^{-10}$ |
| | | | $\mathbf{(1.97\pm0.29)\times10^{-10}}$ | | $\mathbf{(1.55\pm0.27)\times10^{-10}}$ |
| TBMS | Cyclohexane | $0.44\pm0.07$ | $(1.28\pm0.43)\times10^{-10}$ | $0.41\pm0.06$ | $(1.19\pm0.37)\times10^{-10}$ |
| | Heptane | $0.33\pm0.02$ | $(1.16\pm0.15)\times10^{-10}$ | $0.28\pm0.01$ | $(0.98\pm0.08)\times10^{-10}$ |
| | | | $\mathbf{(1.47\pm0.64)\times10^{-10}}$ | | $\mathbf{(1.09\pm0.23)\times10^{-10}}$ |
| Indene | Cyclohexane | $0.55\pm0.04$ | $(1.60\pm0.28)\times10^{-10}$ | $0.33\pm0.03$ | $(0.96\pm0.20)\times10^{-10}$ |
| | Propene | $0.80\pm0.09$ | $(1.84\pm0.47)\times10^{-10}$ | $0.47\pm0.09$ | $(1.09\pm0.44)\times10^{-10}$ |
| | Ethane | $2.91\pm0.12$ | $(1.70\pm0.19)\times10^{-10}$ | $1.68\pm0.22$ | $(0.98\pm0.27)\times10^{-10}$ |
| | | | $\mathbf{(1.71\pm0.31)\times10^{-10}}$ | | $\mathbf{(1.01\pm0.30)\times10^{-10}}$ |

There are no previous determination for the reactions of Cl with AMS, TMBS and indene. Only the rate constant of styrene has been reinvestigated in this study, given an average value of $(1.29\pm0.52)\times10^{-10}$ $cm^3$ molecule$^{-1}$ s$^{-1}$, which is not in agreement with the value determined by Shi and Bernhard (Shi and Bernhard, 1997), $(3.6\pm0.3)\times10^{-10}$ $cm^3$ molecule$^{-1}$ s$^{-1}$. However, the value reported by these authors is similar to the value obtained in our work, $(3.08\pm0.57)\times10^{-10}$ $cm^3$ molecule$^{-1}$ s$^{-1}$, without subtracting the photolysis losses. Although the two rate constants were obtained using the relative rate method under similar reaction conditions, some experimental differences exist and may account for the discrepancy. First, different Cl atom precursors were used in the experiments; $C_2Cl_4O$ was employed in this work, while Shi and Bernhard (Shi and Bernhard, 1997) used $Cl_2$, however we have found that $Cl_2$ reacts in the dark with styrenes and indene. Second, lamps with maximum intensity at 254 nm were employed to photolyzed $C_2Cl_4O$, but aromatic compounds showed losses by photolysis which had to be taken into account in the calculation of the the rate constants with Cl atoms. Furthermore, close to this wavelength Le Person et al. (Le Person et al., 2008) observed large absorption cross-sections ($\sim 10^{-18}$ $cm^2$ molecule$^{-1}$) for the investigated compounds. Third, different reference compounds were employed. Shi and Bernhard (Shi and Bernhard, 1997) used only isobutane as the reference compound,

nevertheless, more than one reference compounds were used in the current work, and the resulting values of k are in fairly good agreement with each other (see Table 1).

As is apparent from Table 1, the difference is small between rate coefficients for Cl atom reaction with the different aromatic compounds. In fact, the lack of an effect of the $CH_3$-substituent group on $\alpha$- and $\beta$-methylstyrene in increasing the Cl atom rate constant over styrene is strange; however, it is known that the increase of the Cl radical rate constant observed in $CH_3$-substituted aliphatic olefins over the unsubstituted ones is related to the increase of the stability going from primary to secondary to tertiary radicals formed as a consequence of an Cl attack. This effect could vanish in aromatic olefins due to the electron delocalization over the aromatic ring, which causes a strong stabilization of the formed benzylic radical. This behavior is also observed for the reactions of styrenes compounds with OH radical (Bignozzi et al., 1981). Although it may also be due to these values are close to the gas kinetic limited value form gas collision theory, what means that the reaction probability is high regardless of collision site and that chemical structure plays a limited role in determining the reaction rate coefficient (Ullerstam et al., 2001).

### 3.2. Mechanistic study

Prior to studying the reactions with Cl atoms a set of experiments was carried out in order to determine the reaction products generated under photolysis of Cl atoms precursor, $CCl_3COCl$, and studied compounds, styrenes and indene. For $CCl_3COCl$ photolysis experiments, phosgene ($COCl_2$), HCl, CO and $CO_2$ have been detected.

The photolysis of studied compounds, apart from detecting CO and $CO_2$, benzaldehyde and formaldehyde have also been identified from styrene, acetophenone and formaldehyde from AMS and benzaldehyde and formaldehyde from TBMS. Therefore, in order to quantify the formation yield in Cl reactions, the photolysis of title compounds were also quantified and sustracted to these yields. The formation yields of these identified products can be derived from the slopes of product concentrations against photolyzed compounds, giving a product yield of around 5% and 8% for benzaldehyde and formaldehyde, respectively from styrene, 4% and 9% for acetophenone and formaldehyde, respectively from AMS and around a 2% for benzaldehyde and formaldehyde from TBMS.

To facilitate the discussion of the results spectra, plots of the concentrations of the products, time-concentration profiles and simulated IR spectra of proposed products are shown in Supporting Information. Only IR spectra and mechanisms are shown in the manuscript.

### 3.2.1- Styrene

Experimentally, CO, $CO_2$, HCl, benzaldehyde ($C_6H_5CHO$), formaldehyde (HCHO), benzoyl chloride ($C_6H_5COCl$) and formyl chloride (HCOCl) were identified as products of UV irradiation of a styrene/$CCl_3COCl$/air mixture. Representative examples of the IR spectra obtained in this reaction are

shown in Figure 2. For clarify, the overall IR spectra have been treated with the atmospheric compensation to suppress the unwanted influence of atmospheric $H_2O$ and $CO_2$ absorption.
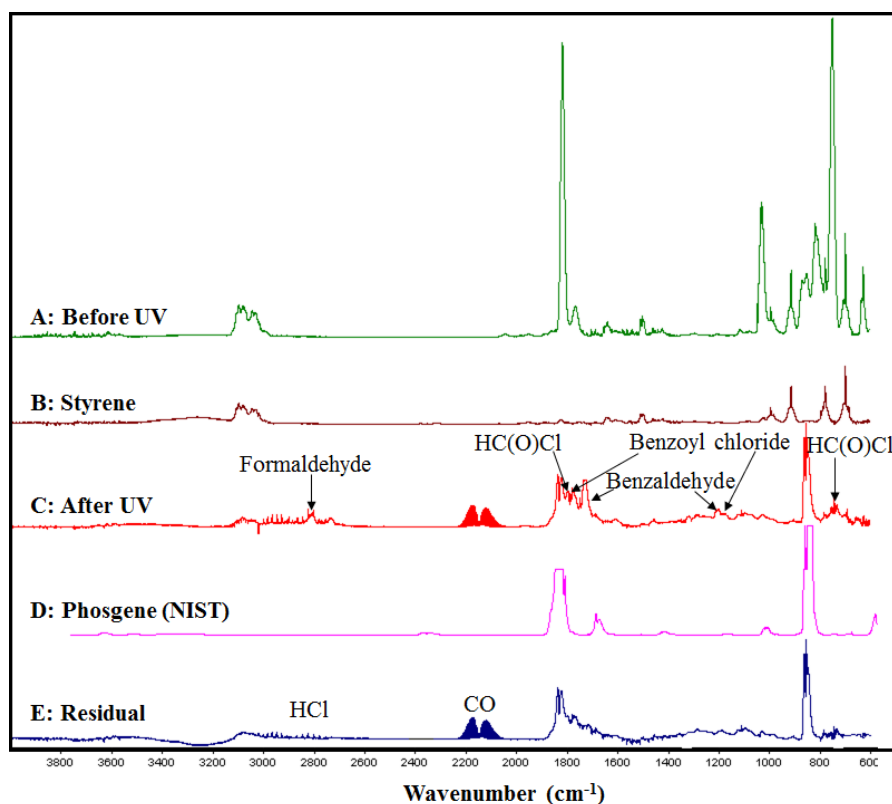


Figure 2.- IR spectra of a mixture of $CCl_3COCl$ and styrene in air before UV irradiation (A) and (C) after UV irradiation where $CCl_3COCl$ and styrene have been subtracted. Figure also shows reference spectra of styrene (B) and phosgene (Trace D, from NIST) and residual (E) which is obtained after subtraction of major identified styrene products from the spectrum in trace B, except HCl, CO and $COCl_2$ which also result from the photolysis of precursor $CCl_3COCl$, as mentioned above.

Concentration-time profiles of styrene and identified products are shown in Figure S1. The concentration of formyl chloride, benzaldehyde, formaldehyde and benzoyl chloride, increases with irradiation time, but in the case of formyl chloride reaches a maximum value and then decreases; this indicates that the compound undergoes secondary reaction. Furthermore, the upward curve of the formaldehyde profile shows that its formation is secondary in nature. Formaldehyde is expected to be produced from multiple sources such as reactions of benzaldehyde with Cl atoms.
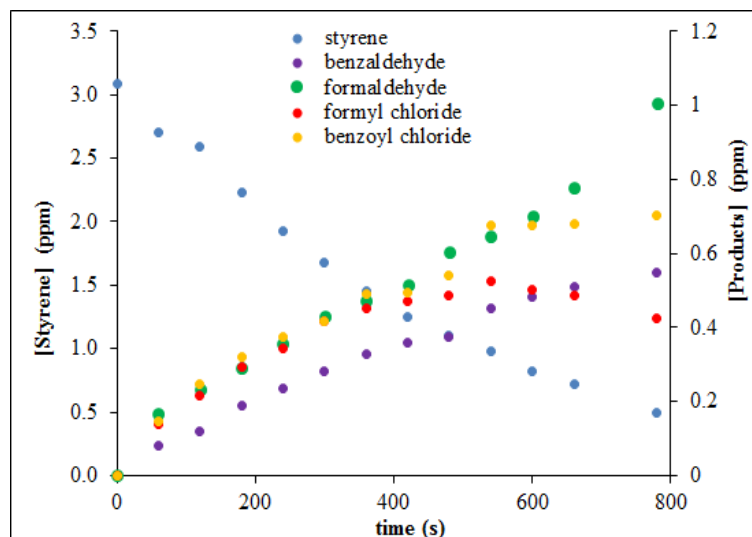
Figure S1.- Time-concentration profiles for the reactant styrene (y-primary axis) and the detected products (y-secondary axis) in the reaction.

Regarding the product quantification, a typical yield plot is shown in Figure S2. The concentration of HCOCl was estimated at 738 cm$^{-1}$ or 1783 cm$^{-1}$ by using a reference calibrated spectrum from the collection of infrared spectra available at the University of Wuppertal, with a value of absorption coefficient of $2.87 \times 10^{-19}$ cm$^2$/molecule and $3.99 \times 10^{-19}$ cm$^2$/molecule, respectively (base 10). From a minimum of three experiments, plots of the yields of products versus the amount of consumed styrene gave a molar benzaldehyde, benzoyl chloride, formyl chloride and formaldehyde yield of 22±3%, 28±6%, 24±4% and 29±2%, respectively. The yield for formaldehyde and benzaldehyde have been corrected due to secondary loss reaction with Cl using k (Cl+formaldehyde)=$7.8 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Niki et al., 1978) and k(Cl+benzaldehyde)=$1.0 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Thiault et al., 2002) by the method outlined in Tuazon et al. (Tuazon et al., 1986). The rate constants with Cl atoms for benzoyl chloride (Caralp et al., 1999) and formyl chloride (Sanhueza, et al., 1975; Niki et al., 1980) have been reported to be fairly low at room temperature, $1.16 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $7.8 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively, so both products have not been corrected for secondary loss. Nevertheless HCOCl readily undergoes thermal decomposition on the walls of reaction chambers, giving CO and HCl as products (Libuda et al., 1990). This fact would justify the decrease in the HCOCl concentration after approximately 500 s of reaction, so only the first few points of a plot of HCOCl as a function of reacted styrene have been used to obtained the yield.
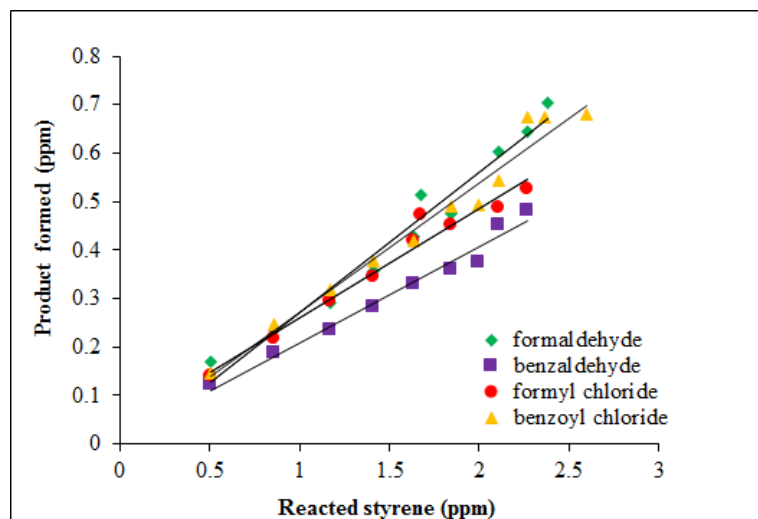
Figure S2.-Plot of the concentrations of the products formed in the reaction of Cl with styrene as a function of the amount of reacted styrene.

The reaction of Cl atoms with unsaturated hydrocarbons can occur by two main pathways: addition to the double bond and, if there are some allylic hydrogens, abstraction and/or addition-elimination (Kaiser and Wallington, 1996a; Kaiser and Wallington, 1996b; Ragains and Finlayson-Pitts, 1997; Stutz et al., 1998). The observed products can be explained by a mechanism mainly by Cl-addition to the double bond of the vinyl group. The absence of oxidation products from the Cl addition to the aromatic ring suggest that Cl attack concerns only the aliphatic moiety of the aromatic molecule. Position β respect to the phenyl group is preferred to position α as the site of the OH attack on the aliphatic chain in the reaction of styrene (Bignozzi et al., 1981; Tuazon et al., 1993), however both carbons of the vinyl group are attacked by Cl atom. This fact suggests that the reactivity of Cl-initiated oxidation is little affected by the substituents and the chemical structure of the unsaturated compounds. This does not occur in the OH additions, so the Cl atoms are, in general, less discriminating than the OH radicals in their reactions with organic compounds (Blanco et al., 2009; Rodriguez et al., 2016). Radical reacts with oxygen to give peroxy radicals (see Figure 3). The peroxy radicals formed can react with other peroxy radicals forming the corresponding alkoxy radicals. Alkoxy radicals in the position β can decompose by C-C bond cleavage producing benzaldehyde and chloromethyl radical ($CH_2Cl$), which can react with oxygen to form formyl chloride, or alkoxy radical can react with oxygen forming 2-chloroacetophenone. 2-Chloroacetophenone could not be quantified since this solid compound was stuck in the reactor´s ducts. Alkoxy radicals in the position α can also decompose by C-C bond cleavage producing formaldehyde and α-chlorobenzyl radical ($C_6H_5CHCl$), giving benzoyl chloride or can react with oxygen forming $C_6H_5CHClCHO$. This last compound is not commercially available, so its identification was carried out using DFT theoretical calculations. We have performed the theoretically-determined IR spectra for products according to the proposed mechanism. Figure S3 compare these calculated IR spectra with the

experimental after UV irradiation. Here we observe the appearance of a peak at $\approx$ 1750 cm$^{-1}$ what is a typical vibrational mode associated to C=O stretching in a C$-$C(O)$-$C structure, and may correspond to $C_6H_5COCH_2Cl$ (S2). Besides, a peak at 2800 cm$^{-1}$ show up in the residual, what is in agreement with the C-H stretching from an aldehyde structure H$-$C=O. These results fit well with the proposed mechanism described in Figure 3 where $C_6H_5CHClCHO$ (S4) and $CHOCH_2Cl$ (S1) may be identified according with the peaks at 2750 and 2800 cm$^{-1}$, respectively.
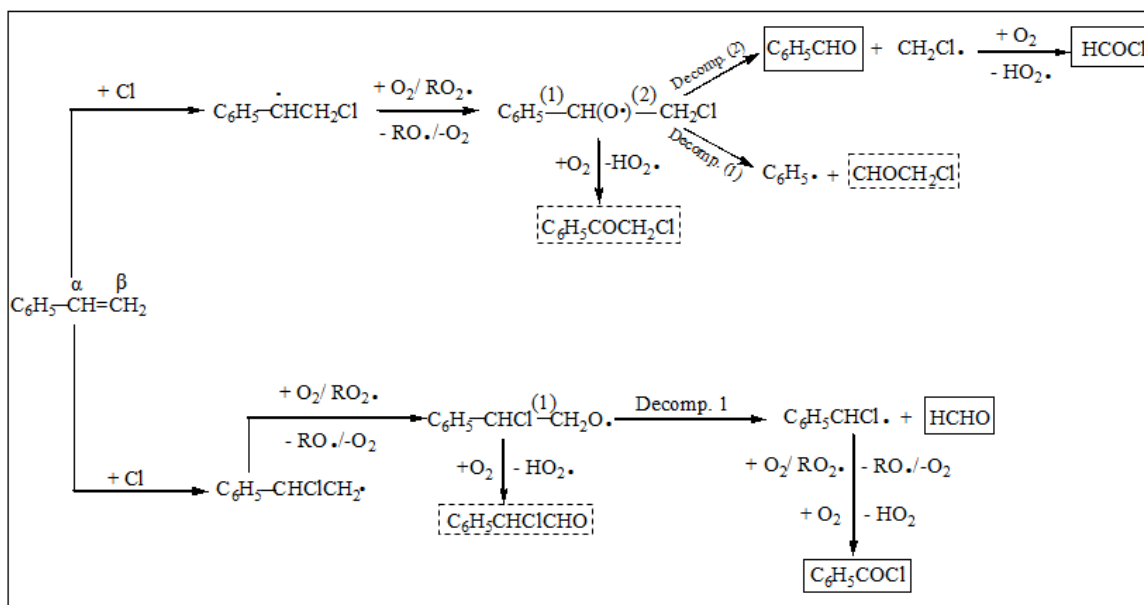


Figure 3.- Simplified mechanism for the Cl-atom initiated oxidation of styrene via addition of Cl to the double bond of the vinyl group. Identified products are shown in solid boxes and theoretically proposed products are shown in dashed boxes.
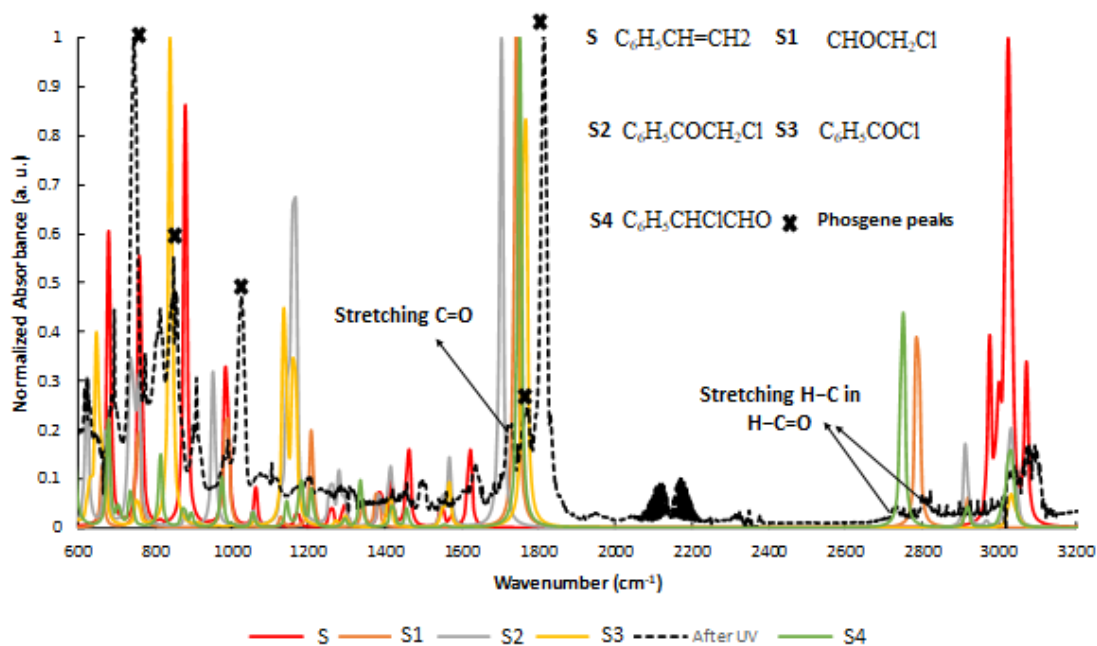
Figure S3.- Simulated IR spectra of proposed products (S) and compared to experimental (dash line). Phosgene peaks are marked as X for a better understanding.

### 3.2.2- AMS

As can be seen in the panel C of IR spectrum (Figure 4) obtained after UV irradiation of a AMS/ $CCl_3COCl$/air mixture, acetophenone ($C_6H_5COCH_3$), formyl chloride and formaldehyde have been identified.
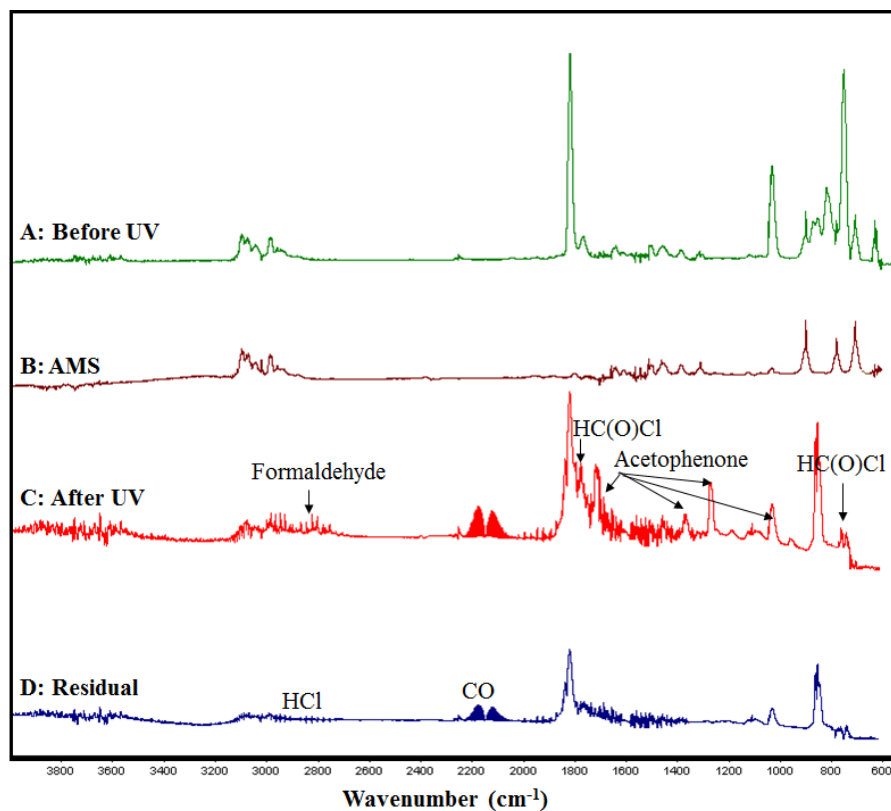
Figure 4.- IR spectra of a mixture of CCl₃COCl and AMS in air before UV irradiation (A) and (C) after irradiation where CCl₃COCl and AMS have been subtracted. Figure also shows reference spectra of AMS (B) and residual (D) which is obtained after subtraction of major identified AMS products from the spectrum in trace C, except HCl, CO and phosgene which also result from the photolysis of precursor CCl₃COCl, as mentioned above.

As can be seen in the time concentration profile (Figure S4) the increase in the product concentrations scale linearly with the loss of AMS supporting that the products are all primary, but as in the case of the styrene reaction, HCOCl reaches a maximum value and then decreases by secondary reactions.
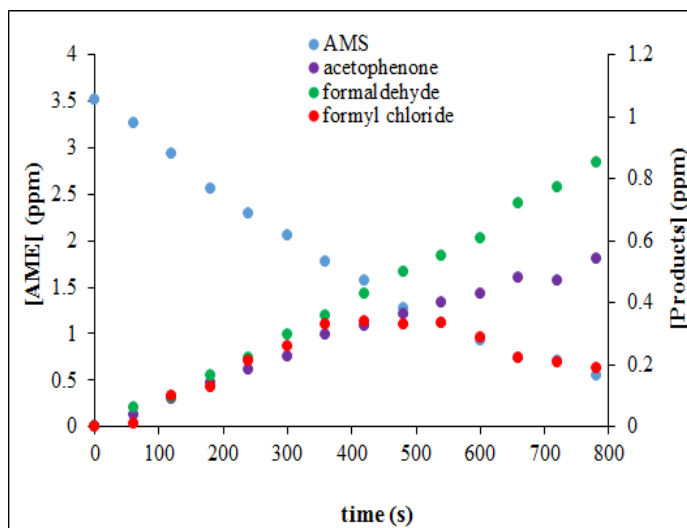
Figure S4.- Concentration–time profile for the decay of AMS (y-primary axis) and the formation of products on irradiation of a AMS/CCl$_3$COCl /air mixture (y-secundary axis).

From the slopes of the plots in the Figure S5 we obtained the yields of formaldehyde, acetophenone and formyl chloride, 26±1%, 18±3% and 20±4%, respectively. Correction of yield for formaldehyde for secondary consumption with Cl, above mentioned, has been made using the method of Tuazon et al. (Tuazon et al., 1986). However, acetophenone and formyl chloride have not been corrected for secondary loss. The rate constant of acetophenone with Cl atoms is not known, so only the first few points of the plot of acetophenone and formyl chloride as a function of reacted AMS have been used to obtained the yields, because if all the points are taken, the yields decrease caused by curvature in the plots from secondary reaction (earlier in the case of HCOCl).
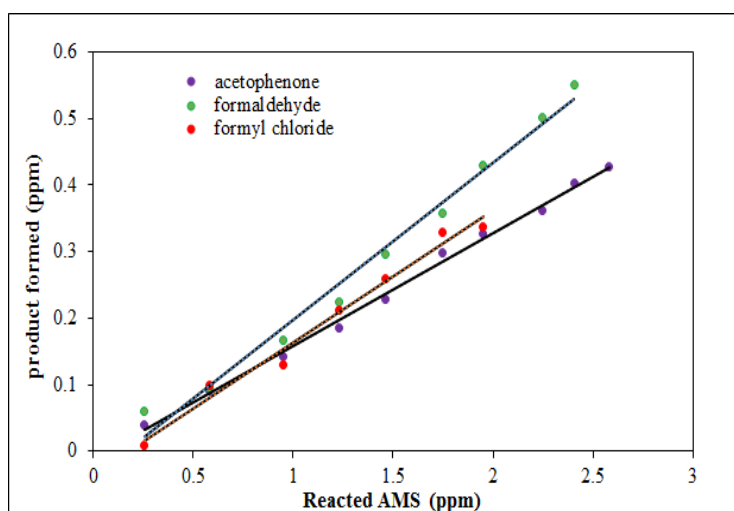
Figure S5.- Plots of the concentrations of the reaction products acetophenone, formaldehyde and formyl chloride as a function of reacted AMS obtained from the irradiation of a AMS/ $CCl_3COCl$/ air reaction mixture.

The observed products can be explained by a mechanism proceeding mainly by the Cl addition to the C=C double bond of the aliphatic chain and followed by fragmentation of the C-C bond of the alkoxy radicals, as styrene reaction (Figure 5), in the same way of the reaction with OH, where acetophenone and formaldehyde were identified (Bignozzi et al., 1981).

In an effort to identify more reaction products from the FTIR residual spectrum, we have carried out DFT theoretical calculations. Figure S6 compare calculated IR spectra with the experimental spectrum after UV irradiation. A peak at $\approx 1700$ cm$^{-1}$ show up in the residual IR spectrum, and may correspond to a vibrational mode associated to C=O stretching in an aromatic ketone structure, C(ar)−C(O)−C. This observation is in agreement with the proposed mechanism described in Figure 5 and therefore may be related to $C_6H_5COCH_2Cl$ (AMS2) and $C_6H_5COCH_3$ (AMS4) products.
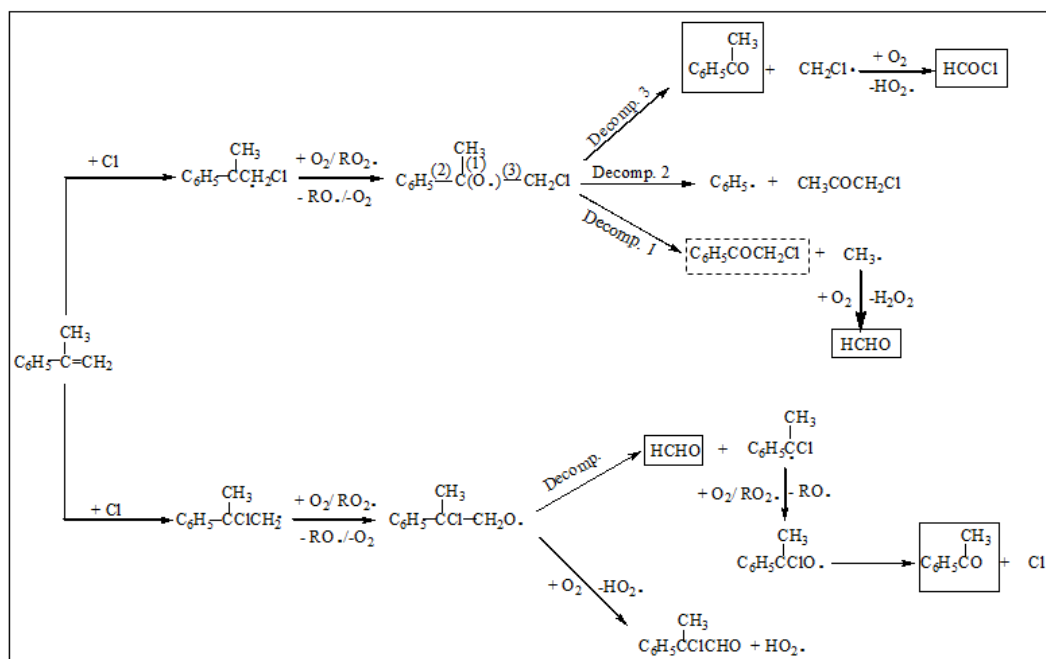


Figure 5.- Proposed mechanism for the reaction of AMS with Cl atoms, in which the identified products are shown in solid boxes and theoretically proposed products are shown in dashed boxes.
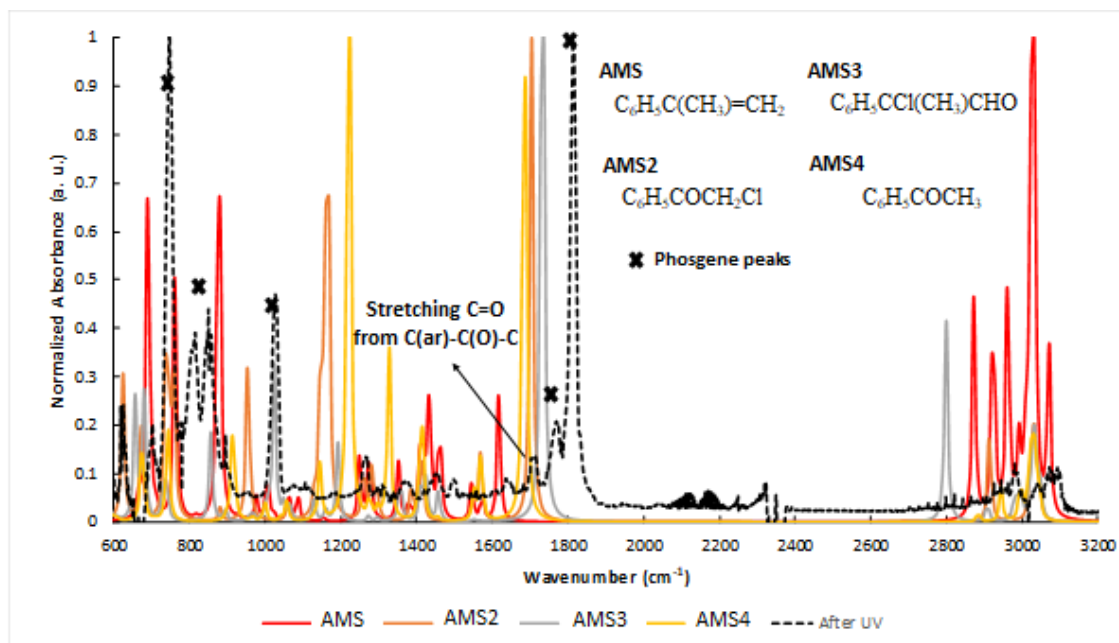
Figure S6.- Simulated IR spectra of proposed products (AMS) and compared to experimental (dash line). Phosgene peaks are marked as X for a better understanding.

### 3.2.3- TBMS

A typical product spectrum obtained after irradiation of TBMS/Cl$_3$CCOCl/air mixture is shown in Figure 6. Major identified and quantified products of this reaction are formaldehyde, benzaldehyde and acetyl chloride (CH$_3$COCl) which come from the addition of Cl atoms to the double bond of the aliphatic side chain of the compound.
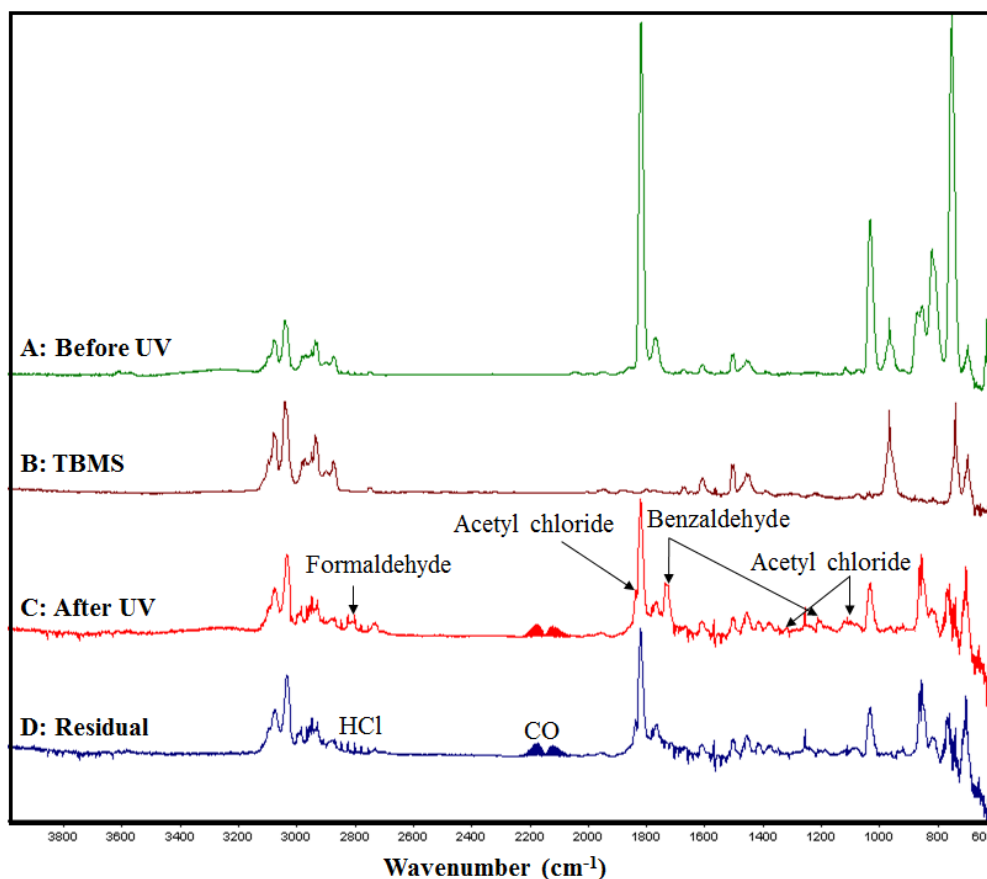
Figure 6.- IR spectra of a mixture of TBMS and Cl₃CCOCl in air before irradiation (A) and (C) after irradiation where CCl₃COCl and TBMS have been subtracted. Figure also shows spectra of TBMS (B) and residual (D) which is obtained after subtraction of major identified TBMS products from the spectrum in trace C (benzaldehyde, fomaldehyde and acetyl chloride).

The time–concentration profiles obtained for reactant and identified products for the reaction of TBMS are shown in Figure S7. Acetyl chloride formation raises in the early stages of the reaction, then decreases due to undergo photodecomposition at 254 nm to generate $CH_3CO$ and Cl atoms (Finlayson-Pitts et al, 1999), since the rate coefficient with Cl atoms has been reported to be fairly low at room temperature, $< 1 \times 10^{-14}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, (Shi, et al., 1993). $CH_3CO$ subsequently decomposes to $CH_3$ and CO (Deshmukht and Hess, 1994). $CH_3$ radical reacts with oxygen to give formaldehyde. This would explain the increase of formaldehyde with irradiation time.
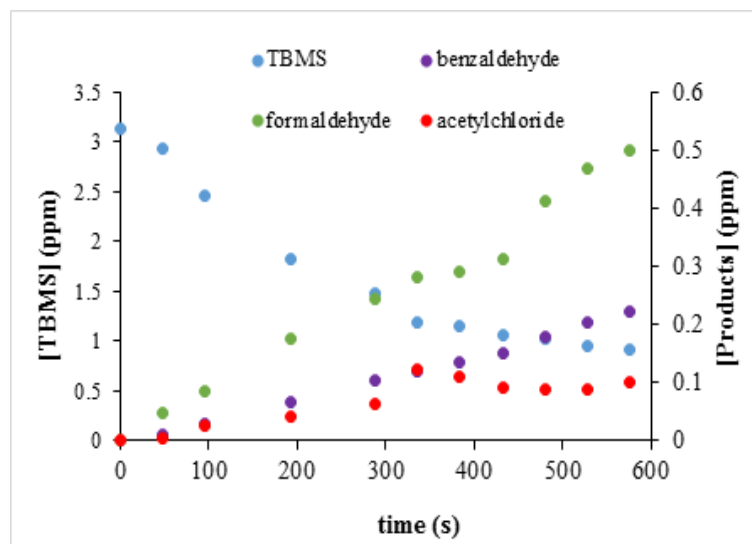
Figure S7.- Time-concentration profiles for the reactant TBMS (y-primary axis) and the detected products (y-secondary axis) in the reaction.

The yields of the reaction products were obtained from the slopes of plots of the amounts of product formed versus the amounts of TBMS consumed (Figure S8) and were estimated to be $14\pm2\%$ for formaldehyde, $7\pm3\%$ for benzaldehyde and $5\pm1\%$ for acetyl chloride. In the residual product spectra (Figure 6, panel D), absorption band can be seen in the regions 1700 cm$^{-1}$ and a strong absorption appears in the 3140-2850 cm$^{-1}$, C-H stretching region, indicating that other products with carbon skeleton are present. In an effort to identify the reaction products observed in the FTIR residual spectrum, we have carried out DFT theoretical calculations. In Figure S9 we can observe a similar behavior to styrene, where a peak at $\approx$ 1700 cm$^{-1}$ show up in the residual IR spectrum. Again, this may be a vibrational mode associated to C=O stretching in a C−C(O)−C structure. This observation is in agreement with the proposed mechanism described in Figure 7 and may be related to TBMS3b ($C_6H_5COCl$), TBMS3c ($C_6H_5CHClCOCH_3$) and TBMS3d ($C_6H_5CHClCOCH_3$) products. $C_6H_5COCl$ can be discarded as product of reaction since it was not experimentally identified. Again, these products confirm a mechanism proceeding by the Cl addition to the C=C double bond of the aliphatic side chain and followed by fragmentation of the C-C bond of the alkoxy radicals, in the same way as styrene and AMS reactions with Cl atoms and as in the case of TBMS+ OH reaction, where the principal oxidation products of TBMS with OH radical have been reported by Bignozzi et al (Bignozi et al., 1981) and were benzaldehyde, formaldehyde and acetaldehyde. The abstraction of olefinic hydrogen by OH was not considered in this study since the activation energy of this process is known to be much higher than that of OH addition to the double bond (Pitts and Finlayson-Pitts, 1975).

Figure S8.- Plot of the concentration of products generated versus the amount of TBMS consumed from the irradiation of a TBMS/CCl$_3$COCl /air reaction mixture.

Based on the reaction products identified, a reaction mechanism is proposed for the reaction of TBMS with Cl atoms (Figure 7).



Figure 7.- Proposed mechanism for the reaction of TBMS with Cl atoms. Identified products are shown in solid boxes and theoretically proposed products are shown in dashed boxes.
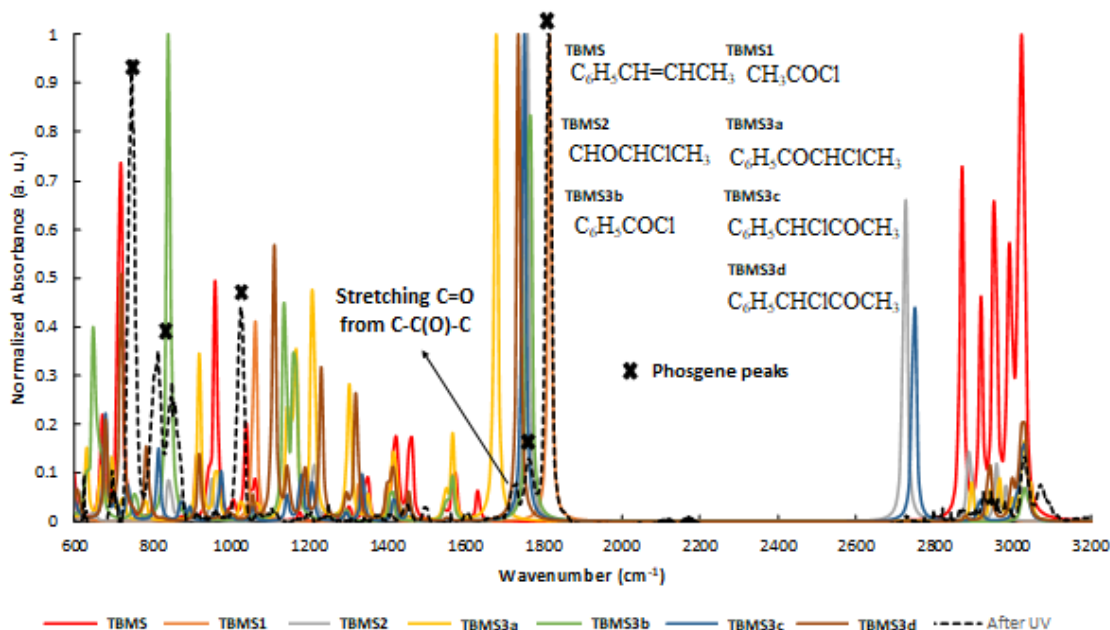
Figure S9.- Simulated IR spectra of proposed products (TBMS) and compared to experimental (dash line). Phosgene peaks are marked as X for a better understanding.

### 3.2.3- Indene

IR spectra obtained during the experiments are shown in Figure 8. Panel A shows the spectrum of indene/$Cl_3CCOCl$ before exposure to radiation, while panel B shows the spectrum of indene and panel C shows the spectrum acquire after lamps irradiation, where indene and $Cl_3CCOCl$ have been subtracted. Concerning the mechanism of this reaction, only a qualitative analysis was carried out due to the absence of commercially available standard. The addition pathway in the 5-member ring is expected to be dominant in the reaction of Cl atom with indene since it is the proposed principal way in the reaction of indene with OH (Kwok and Atkinson, 1995; Kwok et al, 1996). In this sense, the theoretical study give us complementary information to the product analysis on the reaction mechanism.
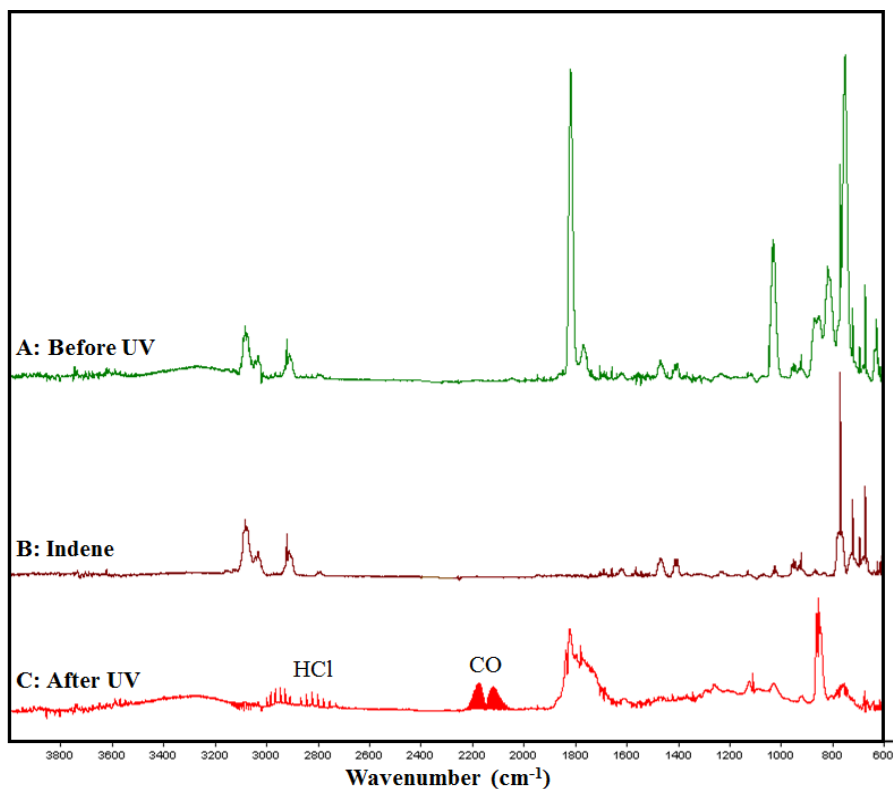
Figure 8.- Panel A shows a mixture of indene and Cl₃CCOCl in air before irradiation, panel B shows the reference spectrum of indene and panel C shows the products spectrum obtained after irradiation on subtraction of indene and Cl₃CCOCl.

In this case, no peaks at 1700 cm$^{-1}$ related to C−C(O)−C structure were observed in Figure S10. However, the presence of products I1 (C₆H₄CHOCH₂COCl), I2 (C₆H₄CHOCH₂CHO) and I3 (C₆H₄CHOCHClCHO) cannot be obviated, ant the typical peaks at 1800 cm$^{-1}$ related to C−C(O)−H structure may be overlapped by the phosgene peak. Besides, a peak at 900 cm$^{-1}$ show up in the experimental spectrum that fits well with the products I1 and I5 (C₆H₅CH₂CHClCHO). Again, this is in agreement with the proposed mechanism described in Figure 9. So, the proposed products can be explained by a mechanism proceeding mainly by the Cl addition to the C=C double bond of cyclopentene ring fused with benzene (see Figure 9) giving a radical, which reacts with oxygen, leading to the formation of peroxy radicals and followed by fragmentation of the C-C bond of the alkoxy radical (in the same way as the other studied compounds).
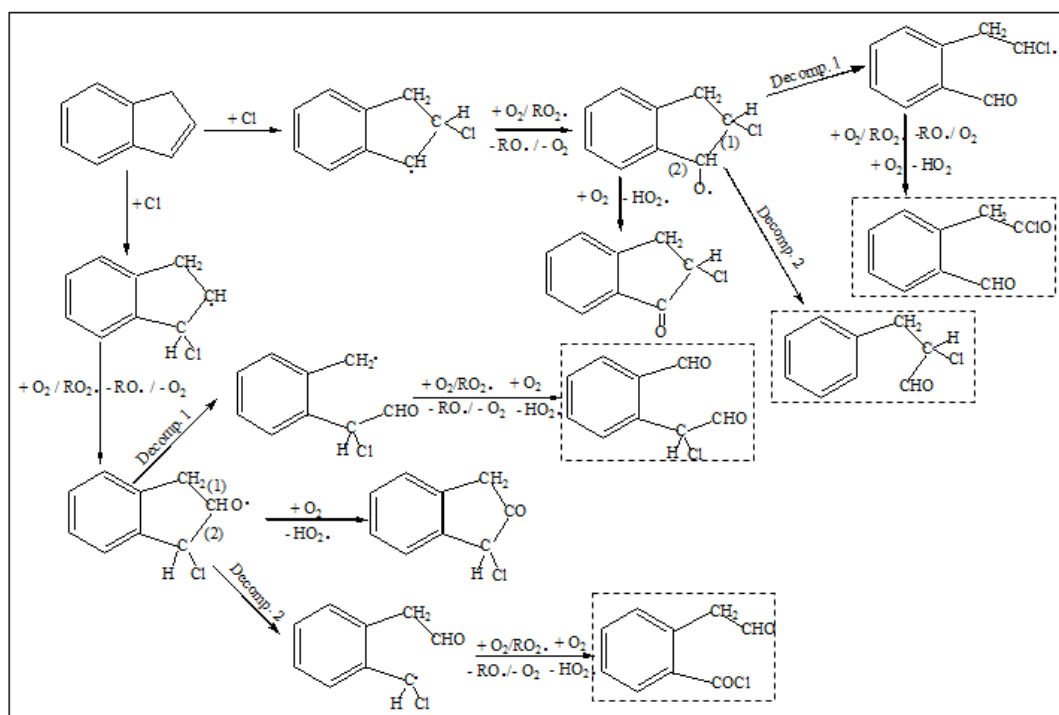
Figure 9.- Proposed mechanism for the reaction of indene with Cl.
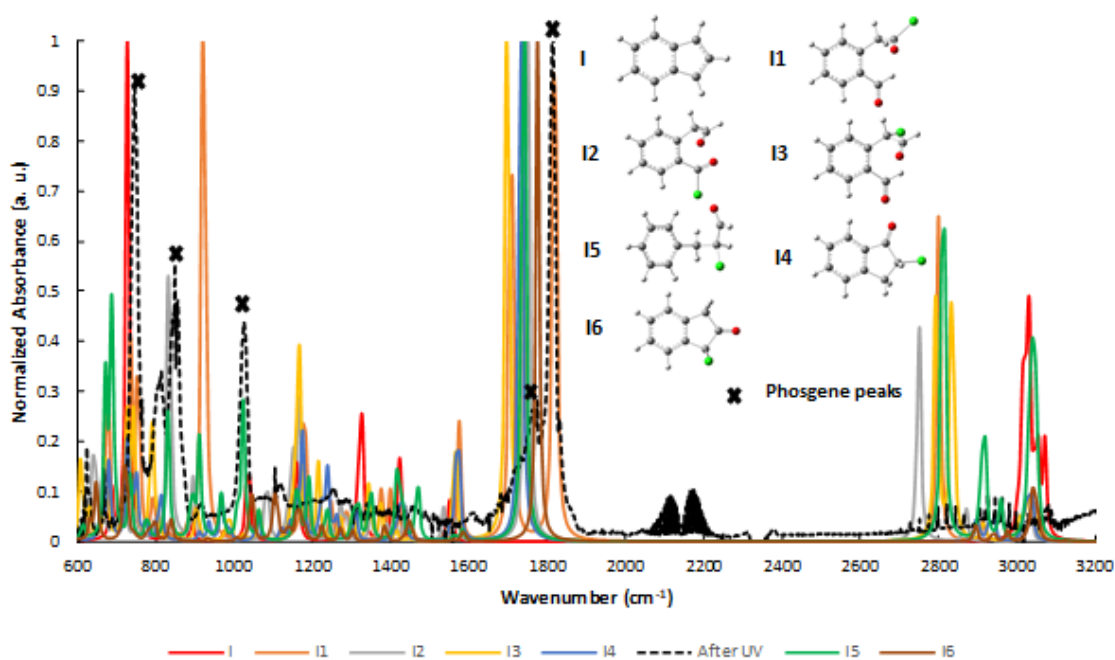


Figure S10.- Simulated IR spectra of proposed products of indene degradation (I) and compared to experimental (dash line). Phosgene peaks are marked as X for a better understanding..

## 4. Atmospheric implications

The tropospheric lifetimes of the investigated aromatics corresponding to each loss pathway ($\tau_x = 1/k_x[X]$, where $[X]$ is the concentration of the tropospheric oxidants) were estimated based on the rate constants measured in this study with Cl atoms and the reported values in the literature for the reactions of OH, $NO_3$ and $O_3$. The following average oxidant concentrations were considered: $5 \times 10^3$ atom $cm^{-3}$ for Cl atoms (Pszenny et al 1993; Wingenter et al 1996), $2 \times 10^6$ radical $cm^{-3}$ for OH radicals (Hein, et al., 1997), $5 \times 10^8$ radical $cm^{-3}$ for $NO_3$ radical (Shu and Atkinson, 1995) and $7 \times 10^{11}$ molecule $cm^{-3}$ for $O_3$ (Logan 1985).

As can be seen in the Table 2, the dominant atmospheric loss processes for the styrenes and indene are clearly their reactions with OH and $NO_3$ radicals. Although lifetimes estimated for the reaction with $O_3$ are somewhat larger than the corresponding to the reactions with OH and $NO_3$ radicals, the role of $O_3$ in the loss of styrenes and indene should not be discarded. In addition, although Cl lifetimes are the highest values indicating that on a global scale, oxidation initiated by Cl atoms will not compete with that initiated by more abundant radicals such as $O_3$, OH and $NO_3$, reactions of Cl atoms are faster than the corresponding ones with OH and $NO_3$ oxidants, which make these reactions potentially important in areas where the atomic chlorine concentrations are high and where oxidation initiated by Cl atoms would be competitive with that initiated by OH radical. In this sense, the production rate of the Cl atoms exceeds the production of OH for 2 or 3 h after sunrise due to the high concentration of $ClNO_2$, precursor of the Cl atoms through its photolysis (Osthoff et al., 2008; Thornton et al., 2010; Mielke et al., 2011; Phillips et al., 2012). Thus, Cl concentrations of $\approx 10^6$ molecules per $cm^3$ have been calculated from the atmospheric concentrations and photolysis rates of $ClNO_2$ in early morning air masses. Under such conditions, Cl degradation of these compounds could be a competitive process compared with $NO_3$ and OH (2.2 h for styrene, 1.8 h for AMS, 2.5 h for TBMS and 2.8 h for indene).

Table 2.- Estimated tropospheric lifetimes of the aromatic compounds studied in this work with Cl, OH, $NO_3$ and $O_3$. k in $cm^3$ molecule$^{-1}$ s$^{-1}$.

| Compound | $k_{Cl}$ | $\tau_{Cl}$ (day) | $k_{OH}$ | $\tau_{OH}$ (hour) | $k_{NO3}$ | $\tau_{NO3}$ (hour) | $k_{O3}$ | $\tau_{O3}$ (hour) |
|---|---|---|---|---|---|---|---|---|
| **Styrene** | $(1.29\pm0.52)\times10^{-10}$ [a] | 17.9 | $(5.87\pm0.15)\times10^{-11}$ [b] | 2.4 | $(1.51\pm0.20)\times10^{-13}$ [b] | 3.7 | $(1.5\pm0.3)\times10^{-17}$ [e] | 26.5 |
| **AMS** | $(1.55\pm0.27)\times10^{-10}$ [a] | 14.9 | $(5.3\pm0.6)\times10^{-11}$ [c] | 2.6 | ---- | | $(1.8\pm0.4)\times10^{-17}$ [e] | 22.0 |
| **TBMS** | $(1.09\pm0.23)\times10^{-10}$ [a] | 21.2 | $(6.0\pm0.6)\times10^{-11}$ [c] | 2.3 | ----- | | ---- | |
| **Indene** | $(1.01\pm0.30)\times10^{-10}$ [a] | 22.9 | $(7.8\pm2.0)\times10^{-11}$ [d] | 1.8 | $(4.1\pm1.5)\times10^{-12}$ [d] | 0.14 | $(16\pm4.0)\times10^{-17}$ [e] | 2.48 |

[a] **this work**

[b] **Atkinson and Aschmann (1988)**

[c] **Bignozzi et al. (1981)**

[d] **Kwok et al. (1997)**

[e] **Le Person et al. (2008)**

In order to evaluate the atmospheric importance of a particular reaction, it is also necessary to consider the reaction mechanism and the products formation. So, the short lifetimes for these reactions indicate that, if released or formed in the atmosphere, they will undergo rapidly degradation in the troposphere giving carbonyl compounds which also play an important role in the atmosphere due to their involvement in photochemical reactions and contribution to aerosol particle formation and growth (Jang and Kamens, 2001); (Kesselmeier and Staudt, 1999).

Concerning the atmospheric fate of the mainly products, the HCOCl of the reaction of styrene and AMS, it is expected to be incorporation into rain, clouds and fog water followed by hydrolysis and removal by wet deposition (Wallington et al., 1994).

In addition, further studies on the products distributions from these reactions need to be performed over NOx levels typically prevailing in the troposphere, in order to gain a better quantitative understanding of their contribution to photo-oxidant formation (such as $O_3$) and precipitation acidity.

In relation to direct effect of styrenes and indene formation/emissions on the SOA formation, our group has recently reported a paper of the ozonolysis of styrene and the reaction conditions leading to their formation (Díaz-de-Mera et al., 2017). It should be interesting to carry out a study of these compounds with Cl under atmospheric conditions in order to establish the contribution of these compounds to SOA formation and therefore, to climate change.

## Conclusion

Measurements of relative rate constants have been carried out on the Cl-atom reactions with styrene, α-methylstyrene, trans-β-methylstyrene and indene at atmospheric pressure and room temperature, using a smog chamber. Since no rate constant data are available in the literature for these compounds (except for styrene), the present work also serves to expand the current kinetics database for Cl-atom reactions with organic compounds. The rate constant for styrene determined in this work is smaller than other reported previously. The origin of the discrepancy could be due to the use of different wavelenght to photolyze the Cl precursor (356 nm to dissociate $Cl_2$ and 254 nm to photolyze $Cl_3CCOCl$). Furthermore, FTIR-based product study in the absence of NOx shows that the main reactions proceed via the initial addition of the Cl to the aliphatic chain of the aromatic molecules. The product yields of reactions were determined to be for styrene: formyl chloride (24±4), benzaldehyde (22±3), formaldehyde (29±2) and benzoyl chloride (28±6) %. For AMS: formyl chloride (20±4), acetophenone (18±3) and formaldehyde (26±1)%. For TBMS: acetyl chloride (5±1), benzaldehyde (7±3) and formaldehyde (14±2)%. The atmospheric lifetimes calculated clearly indicate that the dominant atmospheric loss process for these

compounds is the reaction with the hydroxyl and nitrate radicals, but in coastal areas and in some polluted environments, Cl atom-initiated degradation of these compounds can be significant, if not dominant.

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