

## An overview of the atmospheric reactions between chlorine atoms and some heterocyclic compounds

B. Cabañas<sup>1</sup>, F. Villanueva<sup>2,3</sup>, M. S. Salgado<sup>1,\*</sup>, P. Martín<sup>1</sup>, E. Monedero<sup>4</sup>, and A. Tapia<sup>2</sup>

<sup>1</sup>Departamento de Química Física, Facultad de Ciencias Químicas, <sup>2</sup>Instituto de Tecnologías Química y Medioambiental (ITQUIMA), Laboratorio de Contaminación Atmosférica. Universidad de Castilla La Mancha, Avda Camilo José Cela s/n, 13071 Ciudad Real, <sup>3</sup>Parque Científico y Tecnológico de Albacete, Paseo de la Innovación, 1 02006, <sup>4</sup>Instituto de Investigación de Energías Renovables, Campus Universitario s/n, 02071 Albacete, Spain

### ABSTRACT

The reactions of chlorine (Cl) atoms with volatile organic compounds (VOCs) emitted into the atmosphere are of special interest to understand the role of Cl in the marine and coastal chemistry. In this review we summarize the most recent results obtained in our laboratories concerning the kinetic and products study of the Cl atoms reactions with a series of heterocyclic compounds. We report here kinetic measurements of the reactions of atomic Cl with furan, 2-methylfuran, 3-methylfuran, 2-ethylfuran, 2,5-dimethylfuran, 2-furaldehyde, 3-furaldehyde and 5-methyl-2-furaldehyde. The reactions were studied at 298K and 1 atm using a relative rate technique with GC-FID/MS detection of the organic compounds and different Cl-atom precursors. To assess the atmospheric relevance of these reactions, products of some of the indicated reactions were determined under atmospheric conditions. For products study two different sampling/detection methods have been used: (1) Solid-Phase Micro Extraction, with subsequent analysis by thermal desorption, and gas chromatography with mass spectrometry or flame ionization detection (SPME/GC-MS/FID), and (2) "in situ" with long path Fourier Transform Infrared Spectroscopy (FTIR). The influence of

the structure on the reactivity of these compounds, their reaction mechanisms and the atmospheric implications are also discussed. It is important to mention that we have reported the first kinetics and products measurements of all the considered reactions.

**KEYWORDS:** chlorine-atoms, rate coefficient, relative method, reaction products, tropospheric chemistry

### INTRODUCTION

There has been long-standing interest in the possible role of halogen atoms as tropospheric oxidants [1, 2]. The source of the halogen oxidants is not well established but likely involves chemical production from sea salt accumulated on the ice over the polar night [3]. Generation of halogen oxidants from sea salt would be of little interest for global tropospheric chemistry if they were confined to Arctic sunrise. However, measurements of hydrocarbons and non-radical chlorine species in the marine boundary layer (MBL) at midlatitudes and in the tropics suggest that Cl atoms may be present at least occasionally at concentrations in the range of  $10^4$ - $10^5$  atoms  $\text{cm}^{-3}$  [4-9].

Also in recent years, in relation to continental areas, brick ceramic industries have been the subject of many environmental studies on the origin of pollutants, particularly, F, Cl, and S.

\*Sagrario.salgado@uclm.es

Due to atmospheric emissions by brick factories, local concentrations of HCl and chlorides as high as 40-200 ppm in the emission plume have been reported [10].

Among volatile organic compounds that can react with Cl atoms, furan and its derivatives have to be considered. Furan, alkylfurans and furanaldehydes are a kind of heterocyclic aromatics emitted to the atmosphere as primary pollutants mainly by anthropogenic sources such as combustion of fossil fuels, refuse, plants and, in particular, from the biomass burning [11-14]. They are also produced in the atmosphere as secondary pollutants as products of the photooxidation of hydrocarbons with the structure  $\text{CH}_2=\text{CH}-\text{CR}_1=\text{CHR}_2$ , such as 1,3-butadiene, isoprene and 1,3-pentadiene [15-20] and aromatic compounds such as toluene and *o*-xylene [21]. Finally, they are also emitted to a lesser extent by biogenic sources. In this sense, recent studies show that tropical forest fires are an important source of these compounds [22-23], in particular for 2-methylfuran, 2-ethylfuran and 2,5-dimethylfuran. Agricultural processes [24] and direct emissions from plants [25] are also sources of furans into the atmosphere.

Heretofore, rate coefficients of furan and some derivatives have been reported in the literature for the reaction of OH radical [26-28],  $\text{NO}_3$  [29, 30], Br [31, 32] and  $\text{O}_3$  [26, 29], but there is no data about reactivity of furan, alkylfurans and furanaldehydes with chlorine atoms. For this reason, our research group has been developing in recent years the first kinetic studies of the reactions of chlorine atoms with a series of furans under atmospheric conditions. These studies have derived in several research articles [33-36]. We report in this review the most relevant results of these works that include kinetic measurements of the reactions of atomic Cl with furan, 2-methylfuran, 3-methylfuran, 2-ethylfuran, 2,5-dimethylfuran, 2-furaldehyde, 3-furaldehyde and 5-methyl-2-furaldehyde. Reaction products of furan and alkylfurans have also been investigated.

The goals of the research in our laboratory have been on one hand to elucidate, through laboratory studies, the mechanisms of the reactions of Cl

atoms with furan and its derivatives in sufficient detail so that they can be implemented in atmospheric CT models, and on the other hand to search for unique chlorine-containing compounds, which could serve as “markers” of chlorine atom chemistry in the troposphere. Additionally, results obtained from the degradation mechanism of the alkylfurans might also be used to extrapolate the information obtained here to other compounds containing furan in their structure such as Polychlorinated Dibenzo-Furans (PCDFs), whose gas phase chemistry is difficult to study in the laboratory because of their high toxicity and low volatility.

## EXPERIMENTAL SECTION

### Kinetics measurements

Experiments were carried out at  $(298 \pm 2)$  K of temperature, and atmospheric pressure using a relative rate method. As described in detail elsewhere [37], the decay of the reactant (substrate S) from  $[S]_0$  at time  $t=0$  to  $[S]_t$  at time  $t$ , and the simultaneous loss of the reference compound from an initial concentration of  $[R]_0$  to  $[R]_t$  at time  $t$  is given by equation (I):

$$\ln\left(\frac{[S]_0}{[S]_t}\right) = \frac{k_S}{k_R} \ln\left(\frac{[R]_0}{[R]_t}\right) \quad (\text{I})$$

Thus, a plot of  $\{\ln [S]_0/[S]_t\}$  versus  $\{\ln [R]_0/[R]_t\}$  should be a straight line passing through the origin and whose slope gives the ratio of rate coefficients  $k_S/k_R$ . At each sampling the ratio of concentration of the reference or substrate against the concentration of an internal standard was used in rate coefficients calculations. This method allowed us to minimize the sampling errors. This internal standard was benzene since its reaction rate with Cl is negligible due to its low rate coefficient ( $k_{298} = (1,3 \pm 0,3) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) [38].

Each reaction studied was measured relative to the reaction of one to four reference standards with Cl atoms. Kinetic experiments were carried out using collapsible Tedlar reaction vessels (Adtech) with a volume of 150 L or 200L. Two apertures sealed into the reactor are used to introduce the reactant component mixtures and to allow the sampling.

The reactor was housed in a dark cabinet and surrounded by four lamps with  $\lambda_{\text{max}} = 254 \text{ nm}$  (Philips TUV 36W/ G36T8).

In preliminary experiments, it was found that  $\text{Cl}_2$  could not be used as a chlorine atoms source because it reacts in the dark with the furans (furan, alkylfurans and furanaldehydes). As a result, photolysis at 254 nm of either thionyl chloride ( $\text{SOCl}_2$ ) or trichloroacetyl chloride ( $\text{CCl}_3\text{COCl}$ ) was used to generate atomic chlorine.

Experiments have been described in detail elsewhere [33-36] and only a brief description is given here. The decay of the reactant and reference compound concentrations was followed using gas chromatography (GC) with mass spectrometry, MS, (Shimadzu GC-17A, MS-QP5000) or flame ionization detection, FID (Shimadzu GC-14A or Hewlett Packard 5890 Series II) onto a 30 m TRB-1701 fused silica capillary column. In the experiments with GC-MS the kinetics were followed using the single ion-monitoring (SIM) mode. However previously, a run was performed in the scanning mode to determine the retention time of each reactant. The  $m/z$  values to be monitored by the mass spectrometer were selected taking into account the abundance in the mass spectra of the reference or reactant compounds. The heterocycle and the reference compound were introduced into the reaction bag by injecting a measured amount of these compounds into a stream of the carrier gas (either air or  $\text{N}_2$ ). The usual method to introduce the sample in the analytical system (chromatograph) consists in the transference of the reaction mixture from the reactor to a valve of injection (loop) of the chromatograph by means of a pump. In the case of the furanaldehydes, it was necessary to do one modification in this point because phenomena of condensation of compounds through the transference line were detected. So, solid phase microextraction (SPME) was used as sampling method following the reactions in these cases by GC-FID [35]. For these experiments, reaction samples were collected from the reactor by inserting the fiber (a polymer mixture of divinylbenzene, carboxen, and poly(dimethylsiloxane) (DVB/CAR/PDMS), 50/30  $\mu\text{m}$  SPME, Supelco) into the reactor through a septum positioned at its center.

The fiber was exposed to the gas mixture for 15 min. After sampling, the fiber was inserted into the GC injector for thermal desorption (10 min at  $270^\circ\text{C}$ ) followed by chromatographic separation. Under the experimental conditions it can be considered that the areas of chromatographic peaks, for the heterocycle and the reference compound, at times 0 and  $t$  respectively, are proportional to concentrations. The fiber was used immediately after desorption for the next sampling.

Photolysis was typically carried out in steps of 11-12 s using  $\text{SOCl}_2$  and 2 min using  $\text{CCl}_3\text{COCl}$  (as sources of Cl atoms), followed by turning off the lamps and sampling the reaction mixture. A separate set of runs was also carried out with the individual reference compound or the heterocycles to ensure that the reactions did not produce products with retention times which could interfere with the reactant peaks used in the kinetic analysis. Additionally, all organics were subjected to the 254 nm radiation alone to study the possible photolysis and to ensure that there were no unrecognized reactions occurring in the absence of the Cl atom source. Finally, for each mixture of organics, a number of injections (typically 12 or more) of the unreacted mixture were carried out to obtain an estimate of the precision associated with the measurements in order to use in the error analysis [39]. The standard deviations ( $2\sigma$ ) of these replicate injections were typically in the range 1-4% for the heterocycles and 3-6% for the reference compounds. These measurements also included the losses with the walls of the reaction bag. The reproducibility of the results shows that the wall losses of the reactants were not significant.

Previously to the determination of the rate coefficient  $k_s$ , the possible photolysis of these compounds was studied. Results showed a significant decrease in the concentration of 2-methylfuran, 3-methylfuran, 2-ethylfuran, 2,5- dimethylfuran and 2-furanaldehyde after 10 min UV irradiation at 254 nm. Therefore, when  $\text{CCl}_3\text{COCl}$  is used as Cl precursor (total time of photolysis of 14-22 min), it is necessary to correct the observed second-order rate coefficient in the kinetic experiments in order to obtain the real second-order rate coefficient ( $k_s$ ).

In the photolysis study the equation (II) was used to calculate the constant of photolysis:

$$\ln \frac{[S]_0}{[S]_t} = k_{ph} t \quad (II)$$

where S is the organic compound (reference or substrate compound). So, plotting  $\ln[S]_0/[S]_t$  versus time the constant of photolysis  $k_{ph}$  is obtained from the slope.

Incorporating the photolysis losses into eq. (I), the following relationship is obtained

$$\ln \frac{[S]_0}{[S]_t} - k_{ph} t = \frac{k_S}{k_R} \ln \frac{[R]_0}{[R]_t} \quad (III)$$

That is used in order to obtain the rate coefficient,  $k_S$  of the heterocycle.

When the Cl atom source used is  $\text{SOCl}_2$ , photolysis is carried out in steps of 10 s, being the total time of photolysis 70-110 s. During this time the photolysis undergone by the heterocycles is totally negligible; thus, it was not necessary to make any correction.

Concentration ranges were the following: furan and alkylfurans: 3-13 ppm, furanaldehydes: 1-5ppm, references 1-18 ppm, internal standard: 5-16ppm, Cl atom sources: 32-80 ppm.

The chemicals were as follows: propane and NO (Praxair, 99%), n-nonane (Aldrich, 99.5%), benzene (Panreac, 99%),  $\text{Cl}_2$  (>99.8% Praxair and Messer-Griesheim, 99%),  $\text{ClCOCOC}$  and 2(5H)-furanone (98% Aldrich),  $\text{SOCl}_2$  (>97%, Aldrich) 1-butene,  $\text{CCl}_3\text{COCl}$ , furan, 2-methylfuran, 2,5-dimethylfuran, 2-furaldehyde (furfural), 5-methyl-2-furaldehyde (5-methylfurfural), maleic anhydride and 2-acetylfuran (99% Aldrich), 3-methylfuran (TCI America 98%), 2-ethylfuran (Aldrich, 97%), 3-furaldehyde (>97%, Aldrich), 3-methyl-2(5H)-furanone (Aldrich, 90%), 4-cyclopenten-1,3-dione (Fluka, 99%). All reactants were purified by several trap-to-trap distillations.  $\text{N}_2$  and air (Praxair, ultrahigh purity, 99.999%) were purified by means of an Oxisorb trap and a molecular-sieve trap.

### Products study

The qualitative and quantitative determination of products was performed using two different

experimental set-up (A) a system based on sample pre-concentration, solid phase microextraction (SPME), followed by subsequent separation of species by capillary gas chromatography (GC) and detection of analytes by flame ionization (FID), electron capture (ECD) or mass spectrometry (MS) GC-FID/ECD/MS and (B) a system where the reactants and products were monitored in situ using FTIR spectroscopy [40]. In both cases the experiments were carried out at  $(298 \pm 2)$  K and atmospheric pressure of air. Results presented here correspond only to furan and alkylfurans determination.

A) Experiments using *SPME GC-FID/ECD/MS* have been developed using the same experimental system described previously in the kinetic studies. In this case, samples were collected for 30 min (qualitative analysis) or 15 min (quantitative analysis) by exposing the fiber to the reaction mixture in the Teflon bag. The fiber was then thermally desorbed for 15 min at  $270^\circ\text{C}$  in the heated GC injection port. Reactants and reaction products formed were monitored by gas chromatography with mass spectrometry (electron ionization (EI), and chemical ionization (CI) modes) and ECD for qualitative analysis and using FID for quantitative analysis. In order to determine the concentrations of the different products, the GC-FID response factors of each compound were determined by introducing different known amounts of standards into the Teflon chamber and conducting several replicate analyses with the coated SPME fiber. In cases where it was not possible to obtain a reference sample, only an estimation of the product yield was possible using the effective carbon number method, ECN [41].

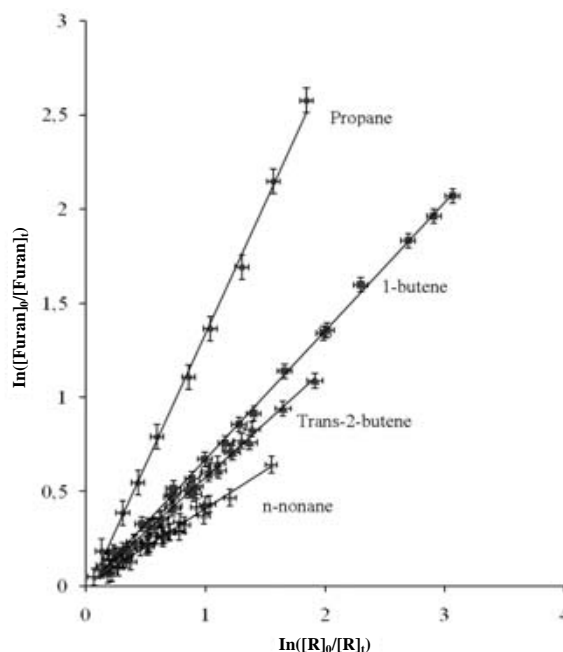
B) Study of products using FTIR has also been described in detail in previous works [34, 42]. Briefly, the in situ FTIR analysis experiments were performed in a 1080 L cylindrical quartz-glass reactor at atmospheric pressure and room temperature. The photolysis of  $\text{ClCOCOC}$  using 10 low-pressure mercury lamps (UV lamps,  $\lambda_{\text{max}} = 254$  nm) and the photolysis of  $\text{Cl}_2$  using 10 superactinic fluorescence lamps (Philips TL 05/40W,  $320 \text{ nm} < \lambda < 480 \text{ nm}$ ,  $\lambda_{\text{max}} = 360$  nm) in the case of furan and 6 UV lamps and 8 VIS lamps in the case of alkylfurans were used to

generate Cl atoms. The reactions between the heterocycles and  $\text{Cl}_2$  were found to be negligible in the quartz-glass reactor at the experimental set-up conditions. The use of molecular chlorine as Cl atoms source therefore avoided potential photolysis at 254 nm of the products generated in the reaction. The concentration-time behaviour of furan and the products were monitored in situ using a multi-reflection White mirror system (5.6 m base length, 498 m total path length) mounted in the reactor and coupled to a FTIR spectrometer (thermo Nicolet Nexus) equipped with a KBr beam splitter and MCT detector. IR spectra were recorded in the  $700\text{--}3700\text{ cm}^{-1}$  spectral range with  $1\text{ cm}^{-1}$  resolution by co-adding 64 interferograms over 60s. In typical experiments 25 spectra were recorded over a period of 25 min with light. A spectral subtraction procedure was used to derive the concentrations of heterocycles and products as a function of the reaction time. Identification and quantification of heterocycles and products was made using calibrated reference spectra produced by introducing a known concentration of an authentic sample of the compound into the reactor or taken from an existing IR spectral library bank [43] or using cross-sections found in the literature data.

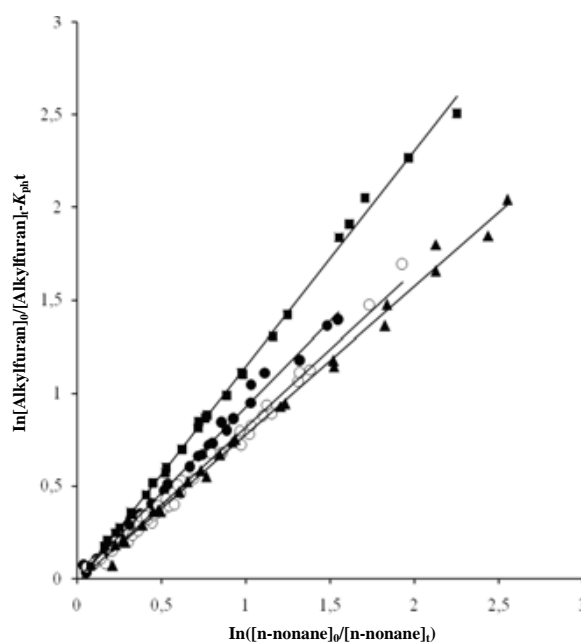
## RESULTS AND DISCUSSION

### Kinetics experiments

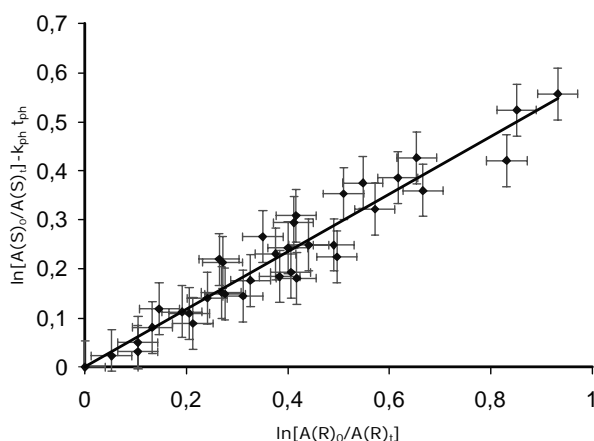
Each reaction studied was measured relative to the reaction of n-nonane as reference standard. In addition, furan reaction was studied employing other three reference compounds (propane, 1-butene and trans-2-butene) and furanaldehydes were also studied with 2-ethylfuran as reference compound. Figure 1 shows the relative kinetic data plotted in the form of equation (I) for Cl+furan, with the four reference compounds employed. Figure 2 shows a plot of Equation III for the reaction of Cl with 2-methyl, 3-methyl, 2-ethyl and 2,5-dimethylfuran taking into account  $k_{\text{ph}}$  previously determined. Figure 3 shows the plot for Cl with 2-furaldehyde. As shown in Figures, the data yield straight lines that pass through the origin (within the experimental error) with a slope of  $k_{\text{s}}/k_{\text{R}}$ . The second-order rate coefficient for the reference compounds used  $k_{\text{R}}$ , are accurately known allowing  $k_{\text{s}}$  to be



**Figure 1.**  $\ln([furan]_0/[furan]_t)$  versus  $\ln([R]_0/[R]_t)$  for the reactions of Cl atoms and furan using different reference compounds.



**Figure 2.** Relative rate plots according to Eq. III for alkylfurans with Cl atoms using  $\text{CCl}_3\text{COCl}$  in  $\text{N}_2$ , (■) 2,5-dimethylfuran, (●) 2-ethylfuran, (○) 3-methylfuran, and (▲) 2-methylfuran. For all, the reference compound is n-nonane. There are no error bars since they are negligible (estimated at 1%).



**Figure 3.** Relative rate plots according to Eq. (III) for 2-furaldehyde with Cl atoms using  $\text{SOCl}_2$  in  $\text{N}_2$ , and 2-ethylfuran as reference compound.

determined. Error bars in figures correspond to a combination of statistical error  $2\sigma$  obtained in regression analysis and uncertainties estimated as explained below.

The relative rate coefficients and the absolute values derived from them for the reactions of heterocycles studied with Cl atoms according to equation I or III are summarized in Table 1. To obtain the ratio  $k_S/k_R$  we used a linear regression that takes into account errors in both the abscissa and the ordinate [39]. The errors in the measured concentrations were calculated by sampling the same mixture repeatedly that corresponds to the random errors, and then its standard deviation is calculated multiplying by the corresponding  $t$ -Student for a degree of confidence of 95%. The total absolute error  $\Delta k_S$  of rate coefficients quoted in the table are a combination of the  $2\sigma$  statistical errors from the regression analysis and the quoted error in the value of the rate coefficient for the reference compound, according to equation (IV):

$$\sigma(k_S) = \sqrt{k_R \sigma(\text{slope})^2 + (\text{slope}) \sigma(k_R)^2} \quad (\text{IV})$$

It can also be observed a good agreement between the values of  $k_S$  determined using different Cl atoms precursors and using different reference compounds. As it can be seen in Table 1, separate sets of experiments were carried out for all organic pairs using air or  $\text{N}_2$  as a carrier gas to test for potential systematic errors due to OH reaction

with the organics and data show that within the error bars there is no significant difference between runs in  $\text{N}_2$  and in air, indicating that interference from OH reaction is negligible.

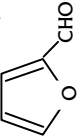
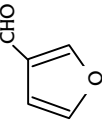
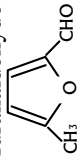
As can also be seen in the table, the large values of the rate coefficients (order of  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) show a great reactivity of Cl towards furan heterocycles. The proposed mechanism for OH-furans reactions [27, 40] is the electrophilic addition to the  $\pi$  system as the main reaction channel. For Cl-furans reactions, we could propose a similar mechanism due to the electrophilic nature of Cl atom. In the case of furan, the attack of the radical for both Cl and OH reactions could happen at C-2 (or C-5) and C-3 (or C-4). Both positions form radicals stabilized by resonance. Nevertheless, the attack at ortho position (C-2 or C-5) leads to a radical intermediate with an additional resonant structure, reason why this position would be more favoured than another one [27].

The larger inductive effect of methyl group increases the reactivity of the cycle in Cl reaction, although the rate coefficient is hardly affected by the length or the position of the alkyl group (compare rate constants of 2/3-methylfuran with 2-ethylfuran). In the case of furanaldehydes, the presence of the aldehydic group ( $-\text{CHO}$ ) involves a negative inductive effect ( $-I$ ) of aromatic ring charge, and what is more important, it supposes a negative conjugated effect and therefore electroacceptor ( $-K$ ), of the conjugated electron pairs of the aromatic ring. So the presence of ( $-\text{CHO}$ ) group produces a deactivation of the aromatic ring toward electrophilic addition process. It is also possible to deduce theoretically that the rate constant of 5-methyl-2-furaldehyde will be higher than those for 3-furaldehyde and 2-furaldehyde, since 5-methyl-2-furaldehyde has also an activating group ( $-\text{CH}_3$ ) and therefore the electrophilic addition will occur in greater extension for this compound than the others. Comparing 3-furaldehyde with 2-furaldehyde the rate constant of 3-furaldehyde is expected to be higher because 3-furaldehyde has only one position deactivated by effect of the  $-\text{CHO}$  group versus two deactivated positions of 2-furaldehyde [35].

**Table 1.** Summary of relative rate coefficients and the absolute values derived from them for the reactions of furan and furan derivatives with chlorine atoms at atmospheric pressure and 298±2 K. The absolute rate coefficients are in units of 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

Organic	Reference	Chlorine Atom Source	Carrier Gas	Detection System	$k_f/k_r(\pm 2\sigma)$	Average $k_f/k_r(\pm 2\sigma)^f$	$k_{298K}(\pm 2\sigma)$	Average $\bar{k}_{298K}$
furan	propane <sup>a</sup>	CCl <sub>3</sub> COCl	N <sub>2</sub>	GC-MS	1.4 ± 0.1		1.9 ± 0.4	
	1-butene <sup>b</sup>	CCl <sub>3</sub> COCl	N <sub>2</sub>	GC-MS	0.68 ± 0.02		2.0 ± 0.3	
	n-nonane <sup>c</sup>	CCl <sub>3</sub> COCl	N <sub>2</sub>	GC-MS	0.41 ± 0.05		2.0 ± 0.2	
	E-2-butene <sup>d</sup>	CCl <sub>3</sub> COCl	Air	GC-MS	0.63 ± 0.05			2.0 ± 0.2 <sup>f</sup>
		SOCl <sub>2</sub>	N <sub>2</sub>	GC-MS	0.58 ± 0.04	0.59 ± 0.03	2.4 ± 0.3	
			Air	GC-MS	0.6 ± 0.1			
			N <sub>2</sub>	GC-MS	0.57 ± 0.1			
2-methylfuran	n-nonane <sup>c</sup>	CCl <sub>3</sub> COCl	Air	GC-MS	0.94 ± 0.06		<b>4.1 ± 0.2</b>	
			N <sub>2</sub>	GC-MS	0.80 ± 0.03	0.85 ± 0.03		
		SOCl <sub>2</sub>	Air	GC-MS	0.99 ± 0.08			
			N <sub>2</sub>	GC-MS	0.91 ± 0.05			
3-methylfuran	n-nonane <sup>c</sup>	CCl <sub>3</sub> COCl	Air	GC-FID	1.0 ± 0.2		<b>4.2 ± 0.3</b>	
			N <sub>2</sub>	GC-FID	0.83 ± 0.05	0.88 ± 0.04		
		SOCl <sub>2</sub>	Air	GC-MS	0.99 ± 0.10			
			N <sub>2</sub>	GC-MS	0.97 ± 0.10			
2-ethylfuran	n-nonane <sup>c</sup>	CCl <sub>3</sub> COCl	Air	GC-FID	1.1 ± 0.2			
			N <sub>2</sub>	GC-FID	0.93 ± 0.05	0.95 ± 0.05	<b>4.6 ± 0.3</b>	
		SOCl <sub>2</sub>	Air	GC-MS	1.1 ± 0.2			
			N <sub>2</sub>	GC-MS	0.9 ± 0.3			
2,5-dimethylfuran	n-nonane <sup>c</sup>	CCl <sub>3</sub> COCl	Air	GC-MS	1.3 ± 0.2			
			N <sub>2</sub>	GC-MS	1.16 ± 0.06	1.17 ± 0.06	<b>5.7 ± 0.3</b>	
		SOCl <sub>2</sub>	Air	GC-MS	1.2 ± 0.2			
			N <sub>2</sub>	GC-MS	1.16 ± 0.1			

Table 1 continued..

2-furaldehyde 	n- nonane <sup>c</sup>	SOCl <sub>2</sub>	N <sub>2</sub>	SPME/GC- FID	0.53 ± 0.03	2.5 ± 0.2
	2-ethylfuran <sup>e</sup>	SOCl <sub>2</sub>	N <sub>2</sub>	SPME/GC- FID	0.59 ± 0.03	2.7 ± 0.2
						<b>2.6 ± 0.3<sup>f</sup></b>
3-furaldehyde 	n- nonane <sup>c</sup>	SOCl <sub>2</sub>	N <sub>2</sub>	SPME/GC- FID	0.66 ± 0.03	3.2 ± 0.2
	2-ethylfuran <sup>e</sup>	SOCl <sub>2</sub>	N <sub>2</sub>	SPME/GC- FID	0.67 ± 0.03	3.1 ± 0.2
						<b>3.1 ± 0.3<sup>f</sup></b>
5-methyl-2-furaldehyde 	n- nonane <sup>c</sup>	SOCl <sub>2</sub>	N <sub>2</sub>	SPME/GC- FID	0.75 ± 0.07	3.6 ± 0.4
	2-ethylfuran <sup>e</sup>	SOCl <sub>2</sub>	N <sub>2</sub>	SPME/GC- FID	0.92 ± 0.04	4.2 ± 0.3
						<b>4.0 ± 0.5<sup>f</sup></b>

<sup>a</sup> rate constant of the reaction Cl + propane = (1.4 ± 0.27) × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [45]<sup>b</sup> rate constant of the reaction Cl + 1-butene = (3.0 ± 0.4) × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [55]<sup>c</sup> rate constant of the reaction Cl + n-nonane = (4.82 ± 0.14) × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [45]<sup>d</sup> rate constant of the reaction Cl + trans-2-butene = (4.0 ± 0.5) × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [55]<sup>e</sup> rate constant of the reaction Cl + 2-ethylfuran = (4.6 ± 0.3) × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [33]<sup>f</sup> Weighted average according to the precision of the measurement (w = 1/σ<sup>2</sup>).



Therefore, we can conclude that the alkyl derivatives (2-methylfuran, 3-methylfuran, 2-ethylfuran and 2,5-dimethylfuran) present alkyl groups that activate the aromatic ring and favour the electrophilic addition implying rate coefficients higher than those for furanaldehydes in its reactivity with chlorine atoms.

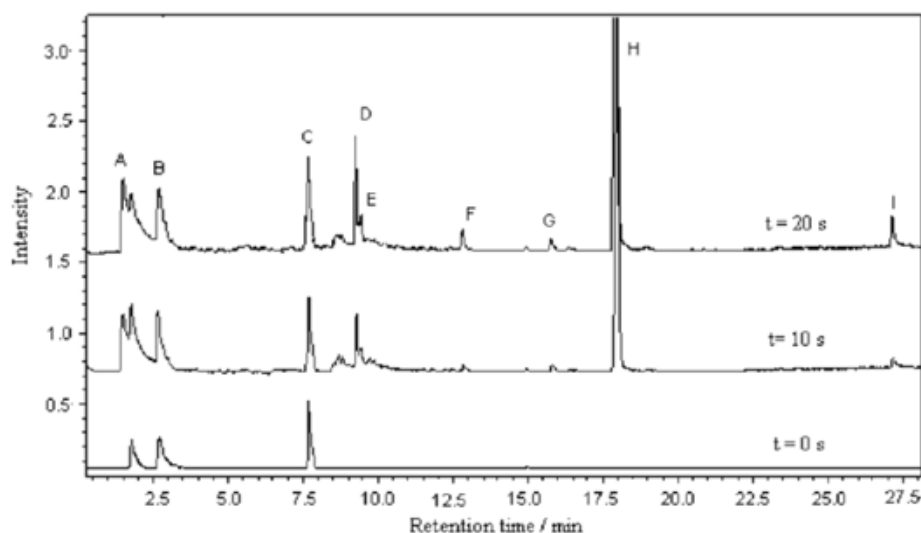
Likewise, it will be expected a rate coefficient for 2-furaldehyde smaller than that of the furan due to the deactivating effect of the  $-\text{CHO}$  group. However, the rate coefficients of 2-furaldehyde and 3-furaldehyde are slightly larger than that of furan. This fact could be explained due to a contribution of the aldehydic abstraction process to the overall rate.

### Products study

The major challenge to identifying the Cl atoms reaction products of furan and alkylfurans (2-methylfuran, 2-ethylfuran and 2,5-dimethylfuran) is the scarcity of commercially available standards. Details of identification and quantification of products of every one of the studied reactions can be found in previous works [34, 36]. Although the rate coefficients obtained in this work indicate that the first step is an electrophilic addition of Cl to one of the  $\text{C}=\text{C}$  of furans, the determination of products are necessary to establish the reaction mechanism.

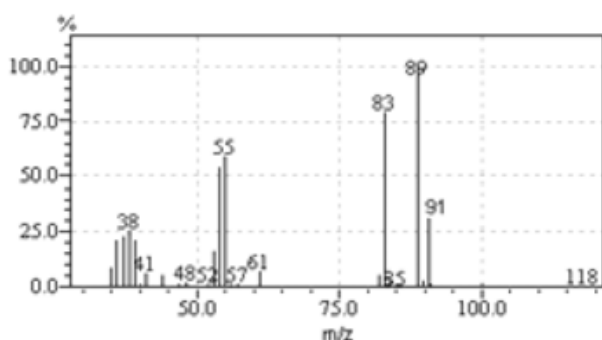
### Furan

Figure 4 shows some typical chromatograms obtained before and after 10 and 20 s photolysis time of a mixture of  $\text{SOCl}_2$  and furan in 1 atm air at room temperature in the absence of  $\text{NO}_x$ . In this figure, we can observe a series of peaks that grow with the photolysis time and can be assigned to reaction products. Peaks A and C are compounds from the Cl-atom source and from the fiber, respectively, peak B is due to furan, peak D is assigned to E-butenedial based on the retention time of a synthesized sample and peak E is tentatively assigned to Z-butenedial, based on the mass spectrum which is similar to the mass spectrum of E-butenedial and by comparison with the mass spectrum of Z-butenedial reported by [44]. Peak F is assigned to maleic anhydride based on the retention time of a standard sample of the compound and its mass spectrum. Peak G is tentatively assigned to 2(3H)-furanone, this compound is not commercially available but it is likely that it has the same retention time and mass spectrum as 2(5H)-furanone. Peak H was tentatively assigned to 5-chloro-2(5H)-furanone based on the mass spectrum (figure 5) and IR spectrum that is presented below, on the gas chromatogram obtained with electron capture detection (ECD) which is especially sensitive to chlorinated compounds and on the tropospheric



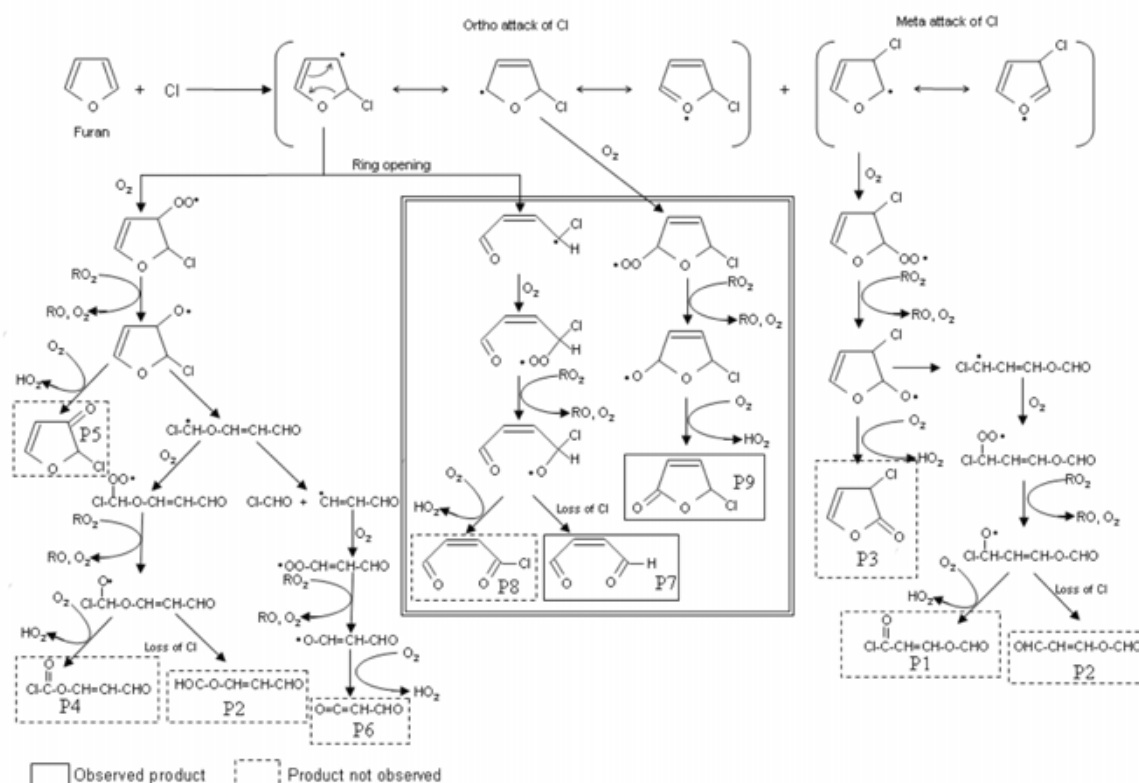
**Figure 4.** Gas chromatograms from reaction mixtures of  $\text{SOCl}_2$  and furan in 1 atm air at room temperature after  $t = 0, 10$  and  $20$  s photolysis period.

reactivity principles (scheme 1). Later, the synthesis of 5-chloro-2(5H)-furanone confirmed its presence. Finally, peak I at 27 min was assigned to 5-hydroxy-2(5H)-furanone based on its mass spectrum and in the synthesis of a similar compound (methyl-hydroxy-furanone) from 3-methylfuran. Figure 6 shows FTIR spectra recorded for different stages of the reaction of furan with Cl: (a) is a spectrum of furan+Cl<sub>2</sub> in air

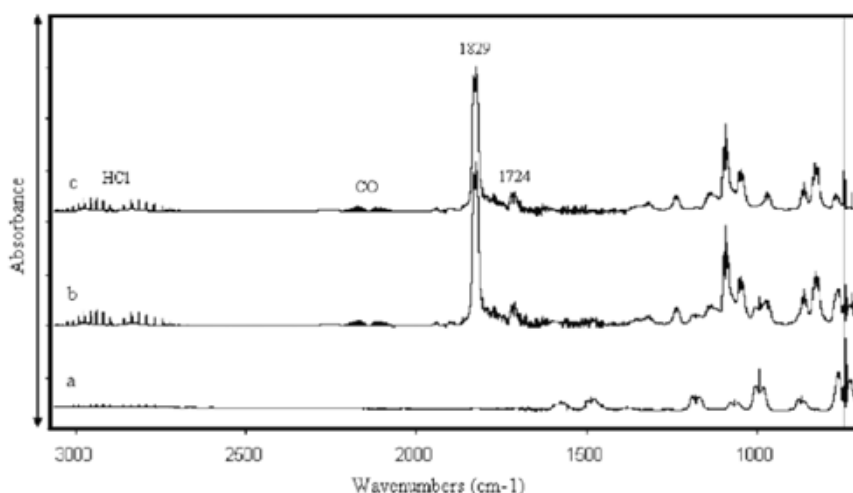


**Figure 5.** EI mass spectrum of 5-chloro-2(5H) furanone.

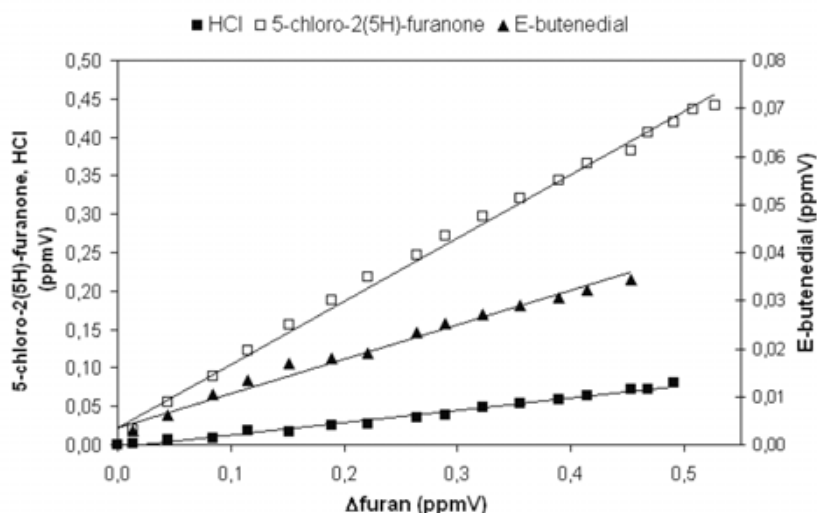
before photolysis, (b) is a spectrum of furan and products after 15 min of photolysis (absorptions from CO<sub>2</sub> has been zeroed due to saturation of the band and those from H<sub>2</sub>O have been subtracted), and (c) is the residual product spectrum after subtraction of furan. In spectrum c, absorption bands due to HCl and CO are readily identifiable, and other tangible features include a weak absorption band around 1724 cm<sup>-1</sup> typical of carbonyl compounds, several absorption bands in the fingerprint region and one very intense band centered at 1829 cm<sup>-1</sup>. The band at 1724 cm<sup>-1</sup> was assigned to E-butenedial based on a comparison with a reference spectrum recorded by [40]. Based on the GC-MS results, the absorption band at 1829 cm<sup>-1</sup> was assigned to 5-chloro-2(5H)-furanone. The lactone 2(5H)-furanone is known to have an intense carbonyl absorption band at 1800 cm<sup>-1</sup> [45], the presence of the Cl atom in 5-chloro-2(5H)-furanone which will inductively withdraw electron density from the ring, would be expected to shift the carbonyl absorption to a higher wavenumber position. Finally, the IR spectrum of



**Scheme 1.** Proposed pathways for the reaction of Cl atoms with furan in 1 atm air at room temperature.



**Figure 6.** (a) FTIR spectrum of furan before photolysis, (b) spectrum of furan and products after 15 min of photolysis, and (c) residual spectrum from (b) after subtraction of furan, H<sub>2</sub>O with the CO<sub>2</sub> absorption zeroed.



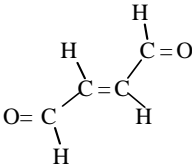
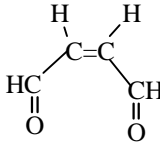
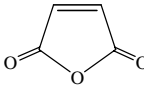
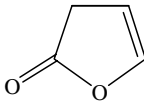
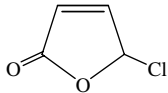
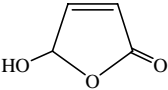
**Figure 7.** Examples of plots of the main reaction product concentrations against the amount of reacted furan obtained by FTIR analysis. Only 5-chloro-2-(5H)-furanone has been corrected for wall loss.

the authentic sample of 5-chloro-2(5H)-furanone confirmed its presence in the reaction of furan with Cl atom.

The concentrations of the reaction products have been calculated using the response factors determined with the procedure outlined in the Experimental Section. The response factor of 2(5H)-furanone was used to estimate the concentration of 2(3H)-furanone, butenedial and 5-chloro-2(5H)-furanone (the synthesis of highly pure samples was not possible) in the SPME-GC- FID technique. In the

case of FTIR, the concentrations of butenedial and 5-chloro-2(5H)-furanone have been estimated using the known absorption coefficients for the structurally related compound 3-hexene-2,5-dione for butenedial [40] and 2(5H)-furanone for 5-chloro-2(5H)-furanone which was measured in the laboratory. Yields for the reaction products have been obtained from the slopes of plots of the concentration of the reaction product formed (corrected for wall loss) versus the amounts of consumed furan. Figure 7 shows an example of this plot.

**Table 2.** Yields of the products observed in the Cl atom oxidation of furan in 1 atm air at room temperature from the SPME-GC-FID and FTIR analyses.

tr (min)	M (CI)	Compound	Structure	Molar Yield/%	
				SPME-GC/MS	FTIR
9.2	84	E-butenedial		$11 \pm 2$	$11 \pm 2^a$
9.4	--	Z-butenedial		$1.6 \pm 0.4$	--
12.8	98	Maleic anhydride		$2.4 \pm 0.3$	$8 \pm 1^b$
15.8	84	2(3H)-furanone		$3 \pm 1$	--
17.9	118	5-chloro-2(5H)-furanone		$58 \pm 7$	$77 \pm 9^a$
27	100	5-hydroxy-2(5H)-furanone		detected	--
--		CO		Not detected	--
--		HCl		Not detected	$21 \pm 3^c$

The errors quoted in table are a combination of the  $2\sigma$  statistical errors from the regression analysis and the errors from the spectral subtraction procedure in the case of FTIR or of the calibration curve in the case of SPME-GC-FID.

<sup>a</sup> Yields are calculated using UV and VIS lamps.

<sup>b</sup> Yield is calculated using only UV lamps.

<sup>c</sup> Yield is calculated using only VIS lamps.

Table 2 shows the yields of the products observed in the Cl atom oxidation of furan from the SPME-GC-FID and FTIR techniques. These yields are the arithmetic average of several experiments. The results show that butenedial and 5-chloro-2(5H)-furanone are the major products of this reaction. Low molar yields of maleic anhydride and 2(3H)-furanone are observed. The FTIR analysis described above suggests that these compounds are mainly secondary products, although there are some indications that maleic anhydride may also be a minor primary product formed together with

5-hydroxy-2(5H)-furanone. Product results clearly indicate that addition of Cl atoms to the double bond of furan is the major pathway. However, the detection of 5-hydroxy-2(5H)-furanone in the GC analyses shows that H-abstraction is also occurring to some extent. It was not possible to calculate the branching ratio for this pathway.

A total carbon mass balance of  $76 \pm 11\%$  is obtained for the detected products in GC-FID experiments and  $90 \pm 15\%$  for the products determined by FTIR. These values must be taken

with caution since the yield could be overestimated [36].

The reaction mechanism proposed for the formation of 5-chloro-2(5H)-furanone and butenedial can be seen in scheme 1. 5-chloro-2(5H)-furanone can be formed from the addition of oxygen to the chlorofuran radical resonance structure with an electron in the five position (scheme 1, centre) that will result in the formation of a chlorofuran peroxy radical which undergo self reaction or reaction with other peroxy radicals in the system to give two chlorofuran alkoxy radicals and molecular oxygen. The chlorofuran alkoxy radical will react with O<sub>2</sub> to form the observed 5-chloro-2(5H)-furanone (P9) and HO<sub>2</sub>. The pathway leading to formation of butenedial most probably involves ring opening of a chlorofuran resonance radical structure with an electron in the C-3 position, followed by addition of oxygen to form a chloro-alkyl peroxy radical that evolves, as explained above, to form two chloro-alkoxy radicals. The elimination of the chlorine atom from the chloro-alkoxy radical formed will result in the formation of E/Z butenedial (P7).

### Alkylfurans

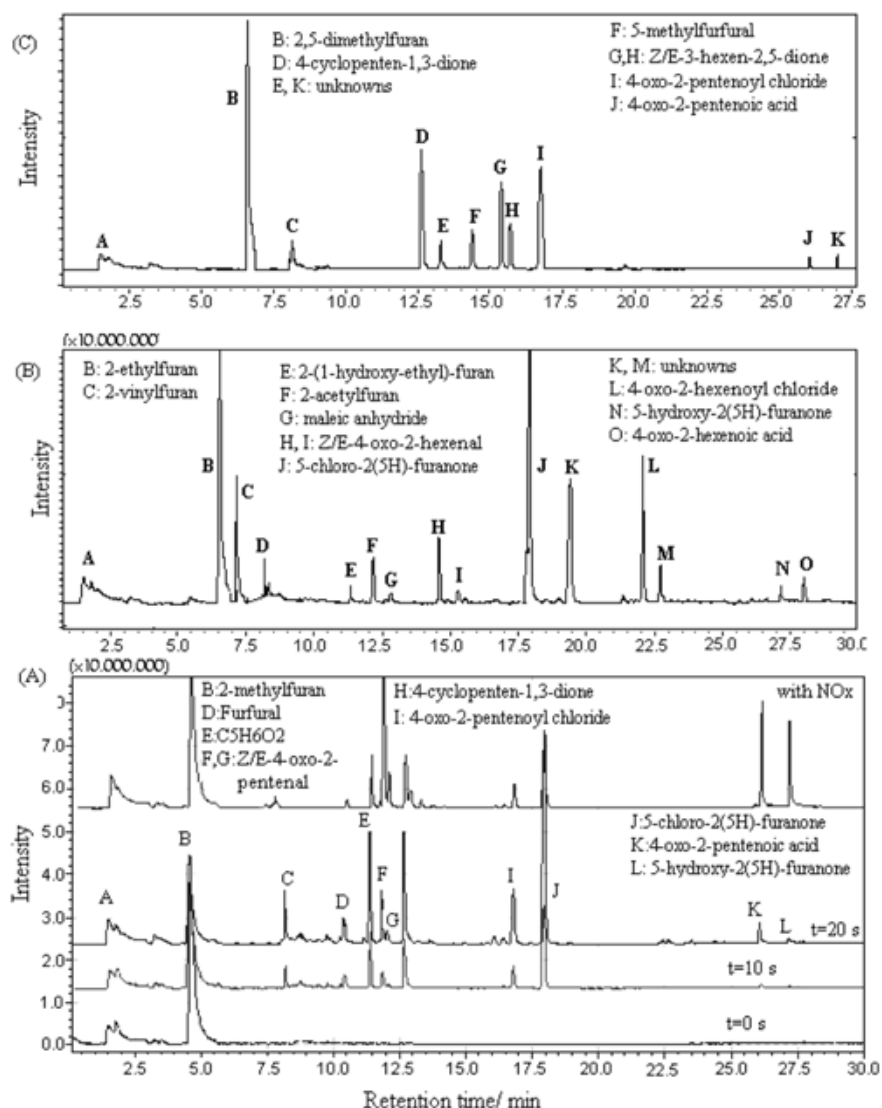
The experimental chromatograms obtained from GC–MS analysis of the reaction samples together with the identified products from the reactions of 2-methylfuran, 2-ethylfuran and 2,5-dimethylfuran with Cl atoms are presented in Figure 8. As it is shown in Figure 8A for 2-methylfuran, the reaction products in the absence and in the presence of NO<sub>x</sub> are similar. The difference consists probably in the yield of the products reflected in the intensity of the peaks (J, K and L). Also in the presence of NO<sub>x</sub>, a small peak can be seen at 12.8 min identified as maleic anhydride [34].

The compounds identified by the mass spectrum and by the retention time of authentic standards are furfural (2-furaldehyde) (peak D), 4-cyclopenten-1,3-dione (peak H) and 4-oxo-2-pentenoic acid (peak K) from 2-methylfuran reaction, 2-acetylfuran (Peak F) and maleic anhydride (Peak G) for 2-ethylfuran reaction and 5-methylfurfural (5-methyl-2-furaldehyde) (Peak F) and 4-oxo-2-pentenoic acid (Peak J)

from 2,5-dimethylfuran reaction and 5-chloro-2(5H)-furanone (Peak J) for both 2-methylfuran and 2-ethylfuran. The rest of the products named in the chromatograms have been identified using their mass spectra and the general tropospheric degradation mechanism proposed in [36]. Thus, 4-oxo-2-pentenoyl chloride has been identified in the reactions of 2-methylfuran and 2,5-dimethylfuran, 4-oxo-2-hexenoyl chloride in the reaction of 2-ethylfuran and 1,4-dicarbonyls such as 4-oxo-2-pentenal, 4-oxo-2-hexenal and 3-hexene-2,5-dione have been identified in the 2-methylfuran, 2-ethylfuran and 2,5-dimethylfuran reactions, respectively.

The residual product IR spectra obtained after 15 min irradiation time of a 2-methylfuran/2-ethylfuran/2,5 dimethylfuran/Cl<sub>2</sub> air mixture are shown in Figure 9. In Figure 9A, absorption bands due to HCl, CO and formaldehyde are readily identifiable for the reaction of 2-methylfuran with Cl atoms. Other tangible feature includes a weak absorption band around 1700 cm<sup>-1</sup> (after subtracting formaldehyde bands) assigned to furfural and 4-oxo-2-pentenal based on a comparison with the reference spectrum. The residual spectrum of 2-methylfuran with Cl atoms after subtraction of all known products mentioned shows a band at 1829 cm<sup>-1</sup> that is assigned to 5-chloro-2(5H)-furanone based on the reference spectrum. The residual spectrum after subtraction of 5-chloro-2(5H)-furanone is shown in Figure 10 and contains a band at 1830 cm<sup>-1</sup> that is typical of the functional group C(O)Cl. This compound could be 4-oxo-2-pentenoyl chloride that was detected by GC–MS in the study of 2-methylfuran and 2,5-dimethylfuran.

From analysis of FTIR spectrum of 2-ethylfuran (Figure 9B) the following products have been identified by a comparison with the reference spectra: HCl, CO, acetaldehyde and 5-chloro-2(5H)-furanone. As in the case of 2-methylfuran after subtraction of all known products, the residual spectrum obtained shows a band at 1830 cm<sup>-1</sup> and it has been tentatively assigned to 4-oxo-2-hexenoyl chloride based on the results obtained for this reaction with SPME/GC–MS analysis. Other products observed as 4-oxo-2-hexenal and 2-acetylfuran have not been quantified due to the lack of the reference spectra.



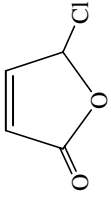
**Figure 8.** Experimental chromatograms and the reaction products identified for the reactions of 2-methylfuran (Fig. 8A), 2-ethylfuran (Fig. 8B) and 2,5-dimethylfuran (Fig. 8C) with chlorine atoms from SPME/GC–MS experiments. Peaks A and C in Fig. 8A and Fig. 8C and peaks A and D in Fig. 8B represent artifact compounds from the chlorine source and from the fiber, respectively.

For 2,5-dimethylfuran (Figure 9C), the FTIR analysis shows the formation of HCl, CO, formaldehyde, 5-methylfurfural and E-3-hexene-2,5-dione. After subtraction of all known products, the residual spectrum obtained could be assigned to 4-oxo-2-pentenoyl chloride, suggestion being based on the results obtained by SPME/GC–MS.

Yields of the main and minor products detected in the reactions of alkylfurans with chlorine atoms using GC-FID and FTIR are summarized in

Tables 3 and 4. For FTIR the concentration of 5-chloro-2(5H)-furanone was calculated from the yield of HCHO in the case of 2-methylfuran and from  $\text{CH}_3\text{CHO}$  in the case of 2-ethylfuran. The formation of formaldehyde and acetaldehyde support the formation of 5-chloro-2(5H)-furanone since HCHO and  $\text{CH}_3\text{CHO}$ , can only be formed from the further reactions of the methyl and ethyl radicals. These radicals are ejected from the ring to form the chlorinated compound. The corrected yield of HCHO and  $\text{CH}_3\text{CHO}$  should give the

**Table 3.** Yields of the main primary products detected in the reaction of 2-methylfuran (2-MF), 2-ethylfuran (2-EF) and 2,5-dimethylfuran (2,5-DMF) with chlorine atoms at room temperature and atmospheric pressure. The errors quoted in table are a combination of the  $2\sigma$  statistical errors from the regression analysis and the errors from the spectral subtraction procedure in the case of FTIR or of the calibration curve in the case of SPME-GC-FID.

Alkylfuran	Reaction Products				Molar Yield/%	
	MW	Rt/min	Name	Structure	SPME/GC-FID	FTIR
2-MF	132	16.7	$R_1 = CH_3$ ; 4-oxo-2-pentenoyl chloride	$R_1-C(O)-CH=CH-C(O)-Cl$	detected <sup>a</sup>	$36 \pm 4^c$
2,5-DMF	132	16.7	$R_1 = CH_3$ ; 4-oxo-2-pentenoyl chloride		detected <sup>b</sup>	$34 \pm 5^e$
2-EF	146	22	$R_1 = CH_2CH_3$ ; 4-oxo-2-hexenoyl chloride		detected <sup>a</sup>	$40 \pm 5^e$
2-MF	118	17.9	5-chloro-2(5H)-furanone		$18 \pm 2^a$	$31 \pm 7^c$
2-EF	118	17.9	5-chloro-2(5H)-furanone		$15 \pm 4^a$	$31 \pm 6^d$
2-MF	--	---	formaldehyde	HCHO	--	$31 \pm 7^c$
2,5-DMF	--	--	formaldehyde		--	$34 \pm 5^e$
2-EF	--	--	acetaldehyde	CH <sub>3</sub> CHO	--	$31 \pm 6^d$
2-MF	--	--	hydrochloride acid	HCl	--	$33 \pm 4^c$
2-EF	--	--	hydrochloride acid		--	$27 \pm 3^d$
2,5-DMF	--	--	hydrochloride acid		--	$66 \pm 8^e$

<sup>a</sup>Average of 5 experiments, <sup>b</sup>Average of 4 experiments, <sup>c</sup>Average of 11 experiments, <sup>d</sup>Average of 5 experiments, <sup>e</sup>Average of 9 experiments.

**Table 4.** Yields of the minor products detected in the reaction of 2-methylfuran (2-MF), 2-ethylfuran (2-EF) and 2,5-dimethylfuran (2,5-DMF) with chlorine atoms at room temperature and atmospheric pressure.

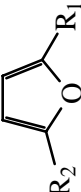
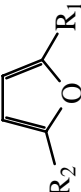
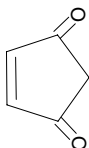
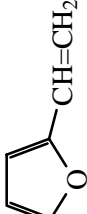
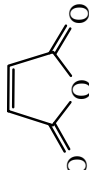
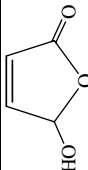
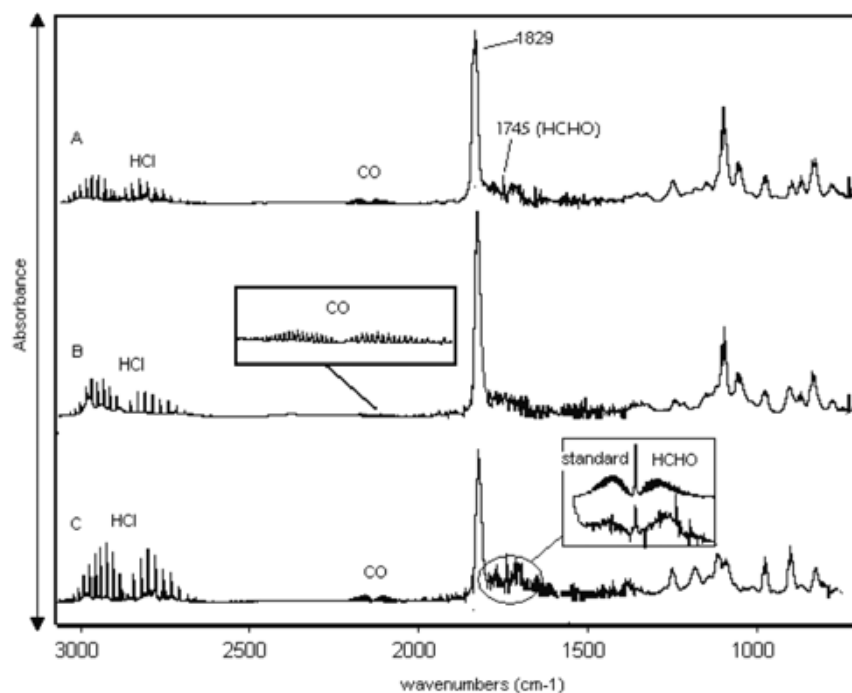
Alkylfuran	Reaction product			Molar Yield/%	
	MW	Rt/min	Name	Structure	FTIR
2-MF	96	10.3	$R_2 = H, R_1 = CHO$ ; furfural		$11 \pm 3^a$
2-EF	110	12.1	$R_2 = H, R_1 = C(O)CH_3$ ; 2-acetylfuran		$2 \pm 1^a$
2,5-DMF	110	14.4	$R_2 = CH_3, R_1 = CHO$ ; 5-methylfurfural		$8 \pm 2^b$
2-MF	98	11.7	$R_1 = H, R_2 = CH_3$ ; 4-oxo-2-pentenal		$1.9 \pm 0.4^a$
2-EF	112	14.6	$R_1 = H, R_2 = CH_2CH_3$ ; 4-oxo-2-hexenal		$4 \pm 1^a$
2,5-DMF	112	15.4	$R_1 = R_2 = CH_3$ ; 3-hexene-2,5-dione		$11 \pm 2^b$
2-MF	96	12.6	4-cyclopenten-1,3-dione <sup>e</sup>		$2.9 \pm 0.6^a$
2,5-DMF	96	12.6	4-cyclopenten-1,3-dione <sup>e</sup>		$8 \pm 1^b$
2-EF	94	7.1	2-vinylfuran		$9 \pm 2^a$
2-MF	98	12.8	maleic anhydride <sup>e</sup>		$3 \pm 1^a$
2-MF	100	27.1	5-hydroxy-2(5H)-furanone		detected <sup>a</sup>



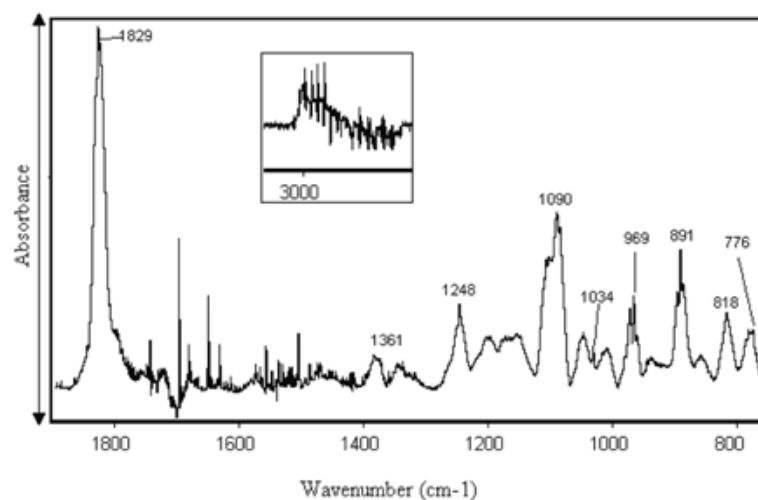
Table 4 continued..

2-EF	100	27.1	5-hydroxy-2(5 <i>H</i> )-furanone	detected <sup>a</sup>	--
2-MF	114	26	R <sub>1</sub> = CH <sub>3</sub> ; 4-oxo-2-pentenoic acid <sup>f</sup>	detected <sup>a</sup>	--
2,5-DMF	114	26	R <sub>1</sub> = CH <sub>3</sub> ; 4-oxo-2-pentenoic acid <sup>f</sup>	detected <sup>b</sup>	--
2-EF	128	28	R <sub>1</sub> = CH <sub>2</sub> CH <sub>3</sub> ; 4-oxo-2-hexenoic acid <sup>f</sup>	detected <sup>a</sup>	--

<sup>a</sup>Average of 5 experiments, <sup>b</sup>Average of 4 experiments, <sup>c</sup>Average of 11 experiments, <sup>d</sup>Average of 5 experiments, <sup>e</sup>Reaction product from secondary reactions of 1,4-dicarbonyl compounds [47], <sup>f</sup>secondary products.



**Figure 9.** Residual product spectra obtained after 15 min irradiation of a 2-methylfuran/2-ethylfuran/2,5-dimethylfuran/ $\text{Cl}_2$  air mixture and subtraction of unreacted alkylfuran and  $\text{H}_2\text{O}$ . A: 2-methylfuran. B: 2-ethylfuran and C: 2,5-dimethylfuran.



**Figure 10.** Residual spectrum from the reaction of 2-methylfuran with Cl atoms after subtraction of all known bands. This spectrum is assigned to 4-oxo-2-pentenoyl chloride.

amount of  $\text{CH}_3$  and  $\text{CH}_3\text{--CH}_2$  being ejected from 2-methylfuran and 2-ethylfuran, respectively and therefore, the yield of 5-chloro-2(5H)-furanone. In the 2,5-dimethylfuran reaction also the formation of HCHO is supportive of the formation

of 4-oxo-2-pentenoyl chloride for the same reason as explained above. The concentration of the acid chlorides (4-oxo-2-pentenoyl chloride in the case of 2-methylfuran and 4-oxo-2-hexenoyl chloride) was estimated applying the Law of Lambert-Beer

for the absorption band at  $1830\text{ cm}^{-1}$  using the known gas phase IR absorption coefficient of the structurally related compound 3-hexene-2,5-dione [46] and  $\text{CH}_3\text{COCl}$  (calculated in the laboratory). For 4-oxo-2-pentenal the concentration was estimated using the IR absorption coefficient of 3-hexene-2,5-dione [46]. The calculated yield of 4-oxo-2-pentenal is the sum of the concentrations of the both trans- and cis- isomers since the reference spectrum is a mixture of them. Taking into account the yields obtained by SPME/GC-FID and FTIR the total carbon mass balance for the alkylfurans is: 86%, for the reaction of 2-methylfuran and 2-ethylfuran and 52% for the reaction of 2,5-dimethylfuran. However, there are many other products which cannot be quantified due to the lack of reference standards. Other types of products, such as aerosols, may be formed in the reaction system but it is unlikely that any significant fraction of the products is being lost to the aerosol phase.

In summary, as it can be seen in table 3, the major primary products were 4-oxo-2-pentenoyl chloride and formaldehyde for the reactions of 2-methylfuran and 2,5-dimethylfuran; 4-oxo-2-hexenoyl chloride and acetaldehyde for the reaction of 2-ethylfuran and 5-chloro-2(5H)-furanone for the reactions of both 2-methylfuran and 2-ethylfuran. Other minor products were 1,4-dicarbonyls such as 4-oxo-2-pentenal, 4-oxo-2-hexenal and 3-hexene-2,5-dione for the 2-methylfuran, 2-ethylfuran and 2,5-dimethylfuran reactions, respectively. From the abstraction pathway, HCl was detected as product for Cl reactions of the three alkylfurans and another compounds detected were the corresponding aldehydes furfural from 2-methylfuran, 2-acetylfuran from 2-ethylfuran and 5-methylfurfural from 2,5-dimethylfuran. The formation of furfural, 2-acetylfuran and 5-methylfurfural confirmed the H-atom abstraction from the alkyl group of 2-methylfuran, 2-ethylfuran and 2,5-dimethylfuran, respectively. Also maleic anhydride and 5-hydroxy-2(5H)-furanone were detected from the abstraction pathway.

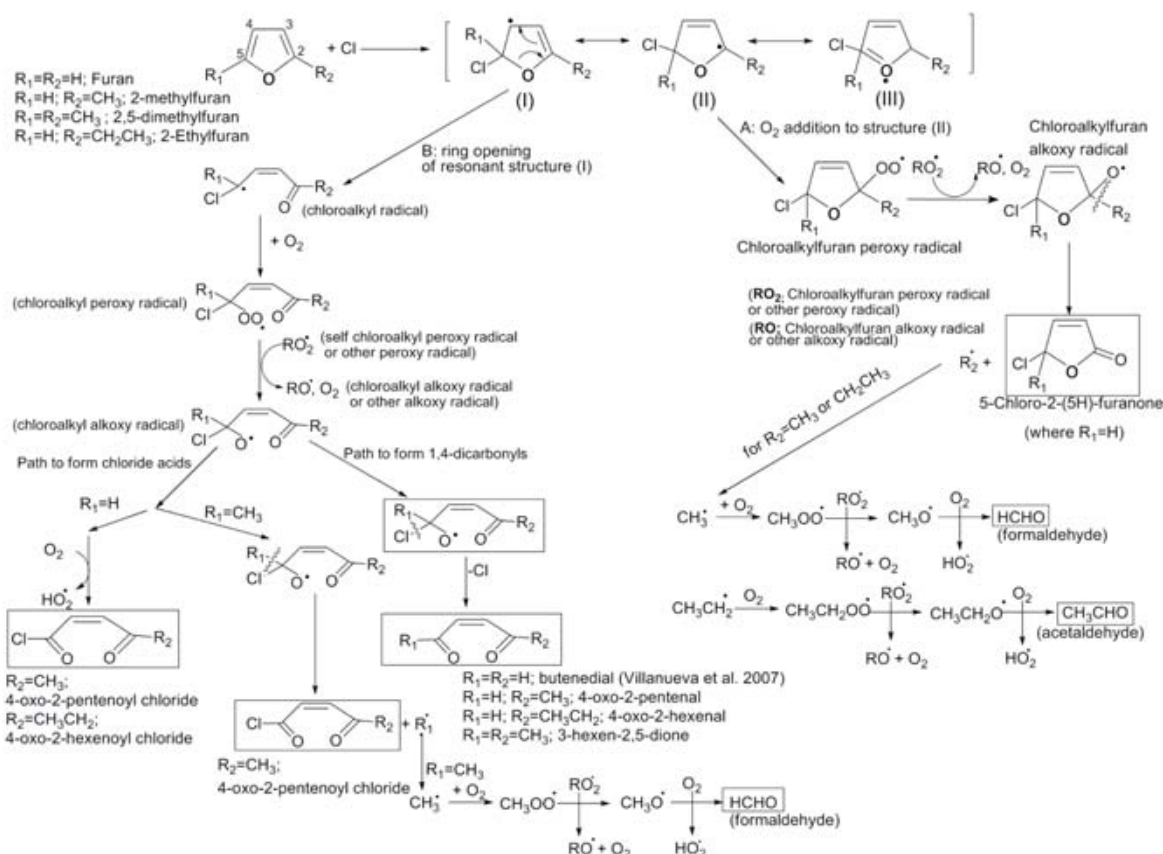
The observed products confirm that addition of Cl atoms to the double bond of the alkylfuran is the dominant reaction pathway, and the proposed mechanisms for these compounds is presented in

scheme 2. The formation of 5-chloro-2(5H)-furanone occurs through the attack of Cl atoms at C-5 position (ortho position) of 2-methylfuran and 2-ethylfuran. This attack involves the formation of a chloroalkylfuran adduct with three resonance structures. The adduct radical (II) reacts fast with  $\text{O}_2$  to yield chloroalkylfuran peroxy radical [37]. In the absence of  $\text{NO}_x$ , the peroxy radicals can either undergo self-reaction or reaction with other peroxy radicals in the reaction system. The dominant pathway is most probably the reaction which leads to formation of two chloroalkylfuran alkoxy radicals and molecular oxygen. The chloroalkylfuran alkoxy radical evolves to form 5-chloro-2(5H)-furanone and a radical that will be  $\text{CH}_3$  from 2-methylfuran and  $\text{CH}_2\text{CH}_3$  from 2-ethylfuran. These alkyl radicals may continue reacting to form formaldehyde and acetaldehyde. 2,5-dimethylfuran is the only alkylfuran in which the formation of chlorinated furanone is not observed probably because the instability of the chloroalkylfuran radical formed in this case that involve the alkyl group and Cl being together at the same carbon (C-5 or C-2).

Two acid chlorides were observed in the different reactions of chlorine atoms with the investigated furans, 4-oxo-2-pentenoyl chloride formed in the reactions of Cl atoms with both 2-methylfuran and 2,5-dimethylfuran and 4-oxo-2-hexenoyl chloride formed in the reaction of 2-ethylfuran with Cl atoms. The pathway leading to formation of acid chlorides most probably involves ring opening of a chloroalkylfuran resonance radical structure with an electron in the C-4 position to form a very stable vinyl radical (resonance structure (I)).

As can be seen in the scheme, the vinyl radical adds  $\text{O}_2$  to form a chloroalkyl peroxy radical and as discussed above this peroxy radical reacts with another peroxy radical (or self-reaction) in the system to form chloroalkyl alkoxy radicals that can evolve through two different paths one to form acid chlorides and other to form 1,4-dicarbonyl compounds.

For 2-methylfuran and 2-ethylfuran reactions (where  $\text{R}_1 = \text{H}$ ), the acid chloride is formed by reaction of the chloroalkyl alkoxy radical with  $\text{O}_2$  while in the reaction of 2,5-dimethylfuran (where  $\text{R}_1 = \text{CH}_3$ ) the chloroalkyl alkoxy radical ejects



**Scheme 2.** Addition mechanism proposed for the reaction of alkylfurans with Cl studied in this work together with the results of furan study of [34]. Path A – all alkylfurans except 2,5-dimethylfuran. Path B – all alkylfurans. (Reprinted from Villanueva, F. *et al.*, *Atm. Environ.*, 41, 8796-8810, Copyright 2007, with permission from Elsevier).

the methyl radical and it can continue reacting to form formaldehyde (path B). The formation of the acid chloride competes directly with the formation of an unsaturated 1,4- dicarbonyl compounds.

Minor reaction products as maleic anhydride, 4-cyclopenten-1,3-dione, 2-cyclohexen-1,4-dione, 4-oxo-2-pentenoic acid and 4-oxo-hexenoic acid, may be explained only as secondary reaction product, probably from the reaction of 1,4-dicarbonyl compounds with Cl atom or as a result of photolysis processes [47-49].

### Atmospheric implications

From the kinetic rate constant data measured at room temperature and at atmospheric pressure together with the average tropospheric concentration of each species of oxidant, the lifetime of furan and its derivatives can be

estimated with respect to their reactions with OH,  $O_3$ ,  $NO_3$  and Cl. The lifetimes were calculated in our previous works [33, 35]. According to the lifetimes obtained in these previous works, the loss of the furans by reaction with Cl atoms are in the range 58-136 hours, whereas for OH reaction are in the range 0.6-23.6 hours. Therefore, the most favoured process for these compounds is daytime reaction with OH. In coastal areas and in the marine boundary layer, where peak concentrations of Cl atoms as high as  $1 \times 10^5$  atoms  $cm^{-3}$  can occur [7], lifetimes calculated with this concentration are ten times lower indicating that Cl atom-initiated degradation of these compounds can be a dominant degradation process. The tropospheric removal of these compounds in the presence of  $NO_3$  radical, assuming a 12 h night time average of  $[NO_3] = 5 \times 10^8$  radicals  $cm^{-3}$  [50] also constitutes a very important sink (lifetime

17 min for furan [51]) that is going to dominate the nocturnal chemistry of furans. Regarding ozone reaction, this oxidant hardly contributes to the degradation of these kinds of compounds since the lifetimes are too large in comparison to the other tropospheric oxidants [26, 29].

In order to evaluate the atmospheric importance of a particular reaction it is necessary to consider the reaction mechanism and the products formation. Products results are consistent with the following remarks and conclusions: Certain chlorinated compounds are formed in the atmosphere from the reaction of Cl atoms with alkylfurans and other parent VOCs and therefore could serve as "markers" in the chemistry of Cl atoms in the troposphere.

With regard to the formation of unsaturated 1,4-dicarbonyls, these species are potentially toxic/ carcinogenic and have mutagenic effects [52]. They are very reactive species once formed in the atmosphere and react further with OH and O<sub>3</sub> [53]. The direct photolysis is also an important loss process of these products [48, 49]. Therefore, these organic compounds may serve as important sources of free radicals, promoting organic aerosols and serve as precursors of carboxylic acids, hydroperoxides and oxidants like O<sub>3</sub>, peroxyacetylnitrate (PAN, CH<sub>3</sub>C(O)OONO<sub>2</sub>) and peroxydicarboxylic acids [54]. Finally, it is clear that the formation of CO<sub>2</sub> takes place even though it could not be quantified. CO<sub>2</sub> could be formed from the reactions of Cl with 1,4- dicarbonyl compounds or with the furanaldehydes.

#### ACKNOWLEDGEMENTS

Esperanza Monedero, Araceli Tapia and Florentina Villanueva thank the Junta de Comunidades de Castilla La Mancha (JCCM) and Ministerio de Ciencia y Tecnología (MCyT), respectively for personal grants. FTIR experiments were performed in the Physikalische Chemie (Wuppertal University) and the authors thank Dr. Ian Barnes and Dr. Iustinian Bejan for their assistance and helpful suggestions. The works in this review were supported by Project PAI06-0042 granted by the JCCM and by CGL2004-03355/CLI granted by the MCyT.

#### REFERENCES

1. Singh, H. B. and Kasting, J. F. 1988, *J. Atm. Chem.*, 7, 261.
2. Chatfield, R. B. and Crutzen, P. J. 1990, *J. Geophys. Res.*, 95, 22319.
3. Impey, G. A., Mihele, C. M., Anlauf, K. G., Barrie, L. A., Hastie, D. R., and Shepson, P. B. 1999, *J. Atm. Chem.*, 34, 21.
4. Keene, W. C., Pszenny, A. A. P., Jacob, D. J., Duce, R. A., Galloway, J. N., Schultz-Tokosm, J. J., Sievering, H., and Boatman, J. F. 1990, *Global Biogeochem. Cycles*, 4, 407.
5. Pszenny, A. A. P., Keene, W. C., Jacob, D. J., Fan, S., Maben, J. R., Zetwo, M. P., Springer-Young, M., and Galloway, J. N. 1993, *Geophys. Res. Lett.*, 20, 699.
6. Singh, H. B., Thakur, A. N., Chen, Y. E., and Kanakidou, M. 1996, *Geophys. Res. Lett.*, 23, 1529.
7. Spicer, C. W., Chapman, E. G., Finlayson-Pitts, B. J., Plastidge, R. A., Hubbe, J. M., Fast, J. D., and Berkowitz, C. M. 1998, *Nature*, 394(6691), 353.
8. Wingenter, O. W., Kubo, M. K., Blake, N. J., Smith, T. W., Blake, D. R., and Rowland, F.S. 1996, *J. Geophys. Res.*, 101, 4331.
9. Wingenter, O. W., Sive, B. C., Blake, D. R. and Rowland, F. S. 1999, *American Geophysical Union*, San Francisco.
10. Galán, E., González, I., and Fabbri, B. 2002, *Atm. Environ.*, 36, 5289.
11. Lipari, F., Dasch, J. M., and Scruggs, W. F. 1984, *Environ. Sci. Technol.*, 18, 326.
12. Toth, L. and Wittkowski, R. 1985, *Chem. Unserer. Zeit.*, 19, 48.
13. Edye, L. A. and Richards, G. N. 1991, *Environ. Sci. Technol.*, 25, 1133.
14. Ciccioli, P., Brancaleoni, E., Frattoni, M., Cecinato, A., and Pinciarelli, L. 2001, *Anal. Lett.*, 34, 937.
15. Ohta, T. 1984, *Bulletin of the Chemical Society of Japan*, 57, 960.
16. Gu, C. E., Rynard, C. M., Hendry, D. G., and Mill, T. 1985, *Environ. Sci. Technol.*, 19, 151.
17. Tuazon, E. C. and Atkinson, R. 1990, *Int. J. Chem. Kinet.*, 22, 591.

18. Ruppert, L., Barnes, I., and Becker, K. H. 1992, Peeters, J. (Ed.), CEC Air Pollution Research Report, 45, 193.
19. Rasmussen, R. A. and Khalil, M. A. K. 1988, *J. Geophys. Res.*, 93, 1417.
20. Ruppert, L. and Becker, K. H. 2000, *Atm. Environ.*, 34(10), 1529.
21. Shepson, P. B., Edney, E. O., and Corse, E. W. 1984, *J. Phys. Chem.*, 88, 4122.
22. Karl, T. G., Christian, T. J., Yokelson, R. J., Artaxo, P., Hao, W. M., and Guenther, A. 2007, *Atm. Chem. Phys.*, 7, 8755.
23. Yokelson, R. J., Karl, T., Artaxo, P., Blake, D. R., Christian, T. J., Griffith, D. W. T., Guenther, A., and Hao, W. M. 2007, *Atm. Chem. Phys. Diss.*, 7, 5175.
24. Lemieux, P. M., Lutes, C. C., and Santoianni, D. A. 2004, *Prog. Energ. Combust*, 30, 1.
25. Ciganek, M., Pisarikova, B., and Zrally, Z. 2007, *Vet. Med-US*, 52, 111.
26. Atkinson, R., Aschmann, S. M., and Carter, W. P. L. 1983, *Int. J. Chem. Kinet.*, 15, 51.
27. Bierbach, A., Barnes, I., and Becker, K. H. 1992, *Atm. Environ. Part A: General Topics*, 26A, 813.
28. Grosjean, D. and Williams II, E. L. 1992, *Atm. Environ. Part A*, 26, 1395.
29. Alvarado, A., Atkinson, R., and Arey, J. 1996, *Int. J. Chem. Kinet.*, 28, 905.
30. Kind, I., Berndt, T., Boege, O., and Rolle, W. 1996, *Chem. Phys. Lett.*, 256, 679.
31. Bierbach, A., Barnes, I., and Becker, K.H. 1996, *Int. J. Chem. Kinet.*, 28, 565.
32. Bierbach, A., Barnes, I., and Becker, K. H. 1999, *Atm. Environ.*, 33, 2981.
33. Cabañas, B., Villanueva, F., Martín, P., Baeza, M. T., Salgado, S., and Jimenez, E. 2005, *Atm. Environ.*, 39, 1935.
34. Villanueva, F., Barnes, I., Monedero, E., Salgado, S., Gómez, M.V., and Martín, P. 2007, *Atm. Environ.*, 41, 8796.
35. Cabañas, B., Tapia, A., Villanueva, F., Monedero, E., Salgado, S., and Martín, P. 2008, *Int. J. Chem. Kinet.*, 40, 671.
36. Villanueva, F., Cabañas, B., Monedero, E., Salgado, S., Bejan, I., and Martín, P. 2009, *Atm. Environ.*, 43, 2804.
37. Finlayson-Pitts, B. J. and Pitts Jr., J. N. 2000, *Chemistry of the Upper and Lower Atmosphere-Theory, Experiments, and Applications*. Academic Press, San Diego.
38. Shi, J. and Bernhard, J. 1997, *Int. J. Chem. Kinet.*, 29, 349.
39. Brauers, T. and Finlayson-Pitts, B. J. 1997, *Int. J. Chem. Kinet.*, 29(9), 665.
40. Bierbach, A., Barnes, I., and Becker, K. H. 1995, *Atm. Environ.*, 29(19), 2651.
41. Scaloni, T. J. and Willis, D. E. 1985, *J. Chromatogr. Sci.*, 23, 333.
42. Barnes, I., Becker, K. H., and Mihalopoulos, N. 1994, *J. Atm. Chem.*, 18, 267.
43. Aldrich library of FT-IR Spectra, 1997, Milwaukee, WI, 5100 094163339X.
44. Berndt, T., Boege, O., and Rolle, W. 1997, *Environ. Sci. Technol.*, 31(4), 1157.
45. Atkinson, R. 1997, *J. Phys. Chem. Ref. Data.*, 26.
46. Tuazon, E. C., Atkinson, R., and Carter, W. P. L. 1985, *Environ. Sci. Technol.*, 19, 265.
47. Bierbach, A., Barnes, I., Becker K. H., and Wiesen, E. 1994, *Environ. Sci. Technol.*, 28, 715.
48. Tang, Y. and Zhu, L. 2005, *Chem. Phys. Lett.*, 409, 151.
49. Tang, Y. and Zhu, L. 2007, *J. Phys. Chem. A*, 111, 925.
50. Shu, Y. and Atkinson, R. 1995, *J. Geophys. Res.*, 100, 7275.
51. Cabañas, B., Baeza, M. T., Salgado, S., Martín, P., Taccone, R., and Martínez, E. 2004, *J. Phys. Chem. A*, 108, 10818.
52. Dumdei, B. E., Kenney, D. V., Shepson, P. B., Kleindiest, T. E., Nero, C. M., Cuppit, L. T., and Claxton, L. D. 1988, *Environ. Sci. Technol.*, 22, 1493.
53. Liu, X., Jeffreis, H., and Sexton, K. G. 1999, *Environ. Sci. Technol.*, 33, 4212.
54. Brasseur, G. P., Orlando, J. J., and Tyndall, G. S. 1999, *Atmospheric Chemistry and Global Change*. Oxford University Press, New York.
55. Orlando, J. J., Tyndall, G. S., Apel, E. C., Riemer, D. D., and Paulson, S. E. 2003, *Int. J. Chem. Kinet.*, 35, 334.