Atmospheric degradation of 3-methylfuran: kinetic and products study

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Abstract

A study of the kinetics and products obtained from the reactions of 3-methylfuran with the main atmospheric oxidants has been performed. The rate coefficients for the gas-phase reaction of 3-methylfuran with OH and NO\textsubscript{3} radicals have been determined at room temperature and atmospheric pressure (air and N\textsubscript{2} as bath gases), using a relative method with different experimental techniques. The rate coefficients obtained for these reactions were (in units cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}): \( k_{\text{OH}} = (1.13 \pm 0.22) \times 10^{-10} \) and \( k_{\text{NO}_3} = (1.26 \pm 0.18) \times 10^{-11} \). The products from the reaction of 3-methylfuran with OH, NO\textsubscript{3} and Cl atoms in the absence and in the presence of NO have also been determined. The main reaction products obtained were chlorinated methylfuranones and hydroxy-methylfuranones for the reaction of 3-methylfuran with Cl atoms, 2-methylbutenedial, 3-methyl-2,5-furanodione and hydroxy-methylfuranones for the reaction of 3-methylfuran with OH and NO\textsubscript{3} radicals and also nitrated compounds for the reaction with NO\textsubscript{3} radicals. The results indicate that in all cases the main reaction path is addition to the double bond of the aromatic ring followed by ring opening in the case of OH and NO\textsubscript{3} radicals. The formation of 3-furaldehyde and hydroxy-methylfuranones (in the reactions of 3-methylfuran with Cl atoms and NO\textsubscript{3} radicals) confirmed the H-atom abstraction from the methyl group and from the aromatic ring, respectively. This study represents the first product determination for Cl atoms and the NO\textsubscript{3} radical in reactions with 3-methylfuran. The reaction mechanisms and atmospheric implications of the reactions under consideration are also discussed.
1. Introduction

3-Methylfuran is a furan derivative that is released into the atmosphere during the combustion of fossil fuels, waste, biomass and from the isoprene degradation (Graedel et al., 1986; Soyer et al., 1988; Atkinson et al., 1989; Bierbach et al., 1994; Andreae and Merlet, 2001). In ambient air, 3-methylfuran has been measured above a rural forested site with mean daytime mixing ratios estimated at 60 ppt and night-time levels of 40 ppt (Montzka et al., 1995).

Mixing ratios of 3-methylfuran were highly correlated with isoprene (Atkinson et al., 1984; Gu et al., 1995; Lee et al., 2005). Isoprene is the most abundant biogenic hydrocarbon emitted into the atmosphere with a global emission rate between 250 and 500 Tg/yr, exceeding that of anthropogenic hydrocarbons (Muller, 1992; Guenther et al., 1995 and 2006; Laothawornkitkul et al., 2009). The reaction of isoprene with OH forms 3-methylfuran in an approximate yield of 3–7% depending presumably on the pressure (Ruppert and Becker, 2000; Lee et al., 2005). Therefore, and due to the high emission rates of isoprene, the potential atmospheric significance of the oxidation products (3-methylfuran) consequently increases.

3-Methylfuran is expected to be very reactive with the main atmospheric oxidants. According to Atkinson et al. (1989), 3-methylfuran may play a role, albeit minor, in the chemical cycles in the lower troposphere. To date very few kinetic studies have been published concerning 3-methylfuran. Indeed, only one value has been reported for the rate coefficient at room temperature for the reaction of the OH radical with 3-methylfuran using a relative technique (Atkinson et al., 1989). Furthermore, two kinetic studies on the reaction of 3-methylfuran with the NO₃ radical have been published (Kind et al., 1996; Alvarado et al., 1996) and these gave two very different values for the rate coefficient. In the case of the reaction with Cl atoms, the rate coefficient reported in the literature was obtained by our research group in a previous work (Cabañas et al., 2005).

With respect to reaction products, the data available in the literature are especially scarce. Only a recent product study for the photooxidation with HONO of 3-methylfuran indicates that 2-methylbutenedial is the main gaseous product of the OH-oxidation of this compound (Gómez Álvarez et al., 2009). A theoretical computational study has also been published for this reaction and the conclusion was that direct
hydrogen abstraction and nucleophilic bimolecular substitution play a minor or negligible role in the overall reaction (Zhang et al., 2008). Therefore, in the work described here rate coefficients for the reaction of OH and NO₃ radicals with 3-methylfuran were determined in order to (i) assess the values previously reported in the literature as they show discrepancies and (ii) to complete the kinetic study of alkylfurans initiated by our research group. Experiments were carried out at (298 ± 2) K and a total pressure of 1 atm using a relative rate method with LOOP/SPME-GC/FID/MS (Loop/Solid Phase Microextraction-Gas Chromatography/Flame Ionization Detection/Mass Spectrometry Detection) and FTIR (Fourier Transform Infrared Spectroscopy) as detection techniques for the organic compounds. Products obtained in the reaction of 3-methylfuran with OH and NO₃ radicals and with Cl atoms were also characterized in order to propose degradation mechanisms for this compound in the atmosphere. This reaction product study was carried out using SPME-GC/FID/MS and FTIR as detection methods.

2. Experimental section

2.1. Kinetic study

Rate coefficient for the gas phase reactions of 3-methylfuran with the atmospheric oxidants, OH and NO₃ radicals, at (298 ± 2) K and ~1 atm of total pressure in synthetic air and N₂, respectively, was determined using a relative rate method. In the experiments the reactions of 3-methylfuran and reference compounds (with rate coefficients $k_S$ and $k_R$, respectively) were monitored in the presence of OH or NO₃ radicals:

23  X + Substrate (S) → products   \( (k_S) \) (R1)

24  X + Reference compound (R) → products \( (k_R) \) (R2)

where X is OH or NO₃

As described in detail elsewhere (Atkinson et al. 1982) the decay of the substrate from $[S]_0$ at time $t = 0$ to $[S]_i$ at time $t$ and the simultaneous loss of the reference compound from an initial concentration of $[R]_0$ to $[R]_i$ at time $t$ is given by Eq. (1):

$$\ln \left( \frac{[S]_i}{[S]_0} \right) = k_S \frac{t}{k_R} \ln \left( \frac{[R]_i}{[R]_0} \right)$$  \hspace{1cm} (1)

Thus, a plot of $\ln ([S]_0/[S]_i)$ versus $\ln ([R]_0/[R]_i)$ should be a straight line passing through the origin and whose slope gives the ratio of rate coefficients $k_S/k_R$. Each reaction
studied was measured relative to the reaction of different reference standards with oxidants X. In the case of 3-methylfuran with NO$_3$, a dilution term was included in Eq. (1) due to the special experimental procedure, which is described below. Therefore, for this reaction the equation required to obtain the rate coefficient is:

$$\ln \left( \frac{[S]_0}{[S]_t} \right) - D_t = \frac{k_s}{k_R} \left( \ln \frac{[R]_0}{[R]_t} - D_t \right)$$  \hspace{1cm} (2)

Where $D_t$ is calculated as $D_t = \ln([I]_0/[I]_t)$ and I is an internal standard.

The relative rate technique relies on the assumption that both the substrate and the reference compound are removed solely by reaction with OH or NO$_3$ radicals. In an effort to verify this assumption, various tests were performed to assess the loss of 3-methylfuran by reaction with precursors of OH and NO$_3$ radicals, photolysis and wall deposition. These processes, which could interfere with the kinetic determinations, were found to be negligible for 3-methylfuran and the selected reference compounds.

The experimental systems and the procedures used in this work are briefly described below. Further details can be found elsewhere (Cabañas et al., 2008; Villanueva et al., 2007; 2009). Only the FTIR system with a 50 L Pyrex glass vessel is described in detail.

Experiments were performed using three analytical systems: gas chromatography with flame ionization detection (GC/FID), gas chromatography with mass spectrometry detection (GC/MS) and Fourier transform infrared absorption spectroscopy (FTIR). In the kinetic experiments carried out with gas chromatography, two evacuable Teflon-coated bags (Adtech) were used – one with a volume of 150 L for the experiments with OH radicals and one of 500 L for the experiments with NO$_3$ in order to minimize the dilution effect of the additions of N$_2$O$_5$. These bags were placed inside a rectangular cage with six VIS lamps ($\lambda_{\text{max}} = 360$ nm) mounted on the walls. A system based on sample preconcentration, the solid phase microextraction technique (SPME) and a heated loop of 1 cm$^3$ capacity mounted in a six way valve were used as sampling methods. In the first case the samples were collected for 15 min by exposing a 50/30 mm DVB/CAR/PDMS fibre to the reaction mixture in the Teflon bag. The fibre was then thermally desorbed for 10 min at 270 ºC in the heated GC injection port. In the second case the reaction mixture was slowly pumped through the sampling loop to ensure that it was thoroughly flushed and then allowed to come to equilibrium with a reaction chamber pressure of 1 atm prior to injection. The concentrations of 3-
methylfuran and the reference compounds were followed by means of capillary gas chromatography and detection by FID or MS. In all experiments a capillary column (30m × 0.32mm id × 1.0 μm film thickness, Tracsil TRB-1701, Teknokroma) was used to separate the compounds. The chromatographic conditions used for the analysis were as follows: injector, 270 ºC; detector, 250 ºC, the temperature program was from 40 ºC (4 min) to 120ºC (17 min) at a rate of 25 ºC min$^{-1}$.

The in situ FTIR analysis of 3-methylfuran with OH and NO$_3$ radicals was carried out in a 50 L Pyrex glass reaction chamber at a total pressure of approximately 1 atm and (298 ± 2) K in synthetic air. The reactants were injected into the reaction chamber using a vacuum line. A pumping system consisting of a rotary pump (Varian DS 302) was used to evacuate the reactor after every experiment. The photolysis system consisted of eight actinic fluorescent lamps ($\lambda_{\text{max}} = 360$ nm) spaced evenly around the reaction chamber. The chamber was equipped with a White-type multiple-reflection mirror system (Saturn Series Multi-Pass cells) with a base length of 1.35 m for sensitive in situ long path absorption monitoring of reactants and products in the IR spectral range 4000–650 cm$^{-1}$. The White system can operate at 72 traverses, giving a total optical path length of 200 m. The IR spectra were recorded with a resolution of 1 cm$^{-1}$ using a Thermo Nicolet 5700 FT-IR spectrophotometer equipped with a KBr beam splitter and a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector. Typically, for each spectrum, 60 interferograms were co-added over 2 min and approximately 30 such spectra were recorded per experiment. Hydroxyl radicals were generated in the presence of NO by the photolysis of CH$_3$ONO in air (Atkinson et al., 1981) at wavelengths of 360 nm using the VIS lamps.

The techniques and the reference compounds used in the reactions of 3-methylfuran with OH and NO$_3$ radicals are listed in Table 1.

In the experiments performed with LOOP/GC-MS, benzene was used as the internal standard. The reactant mixtures were photolyzed for 0.5–2.0 min and a gas chromatogram or an IR spectrum of the chamber contents was recorded. This photolysis-sampling procedure was repeated until around 54–93% depletion of the 3-methylfuran and 41–83% depletion of the reference compound were achieved. Typically six to seventeen photolysis-sampling steps were carried out during each experiment.
Nitrate radicals were generated in situ in the dark by the thermal decomposition of N₂O₅ (Atkinson et al., 1984; Atkinson et al., 1988). During GC-FID experiments successive additions of N₂O₅ (2.5 × 10¹³–1.1 × 10¹⁴ molecule cm⁻³) were performed. Sampling was carried out approximately 7 min after the addition of N₂O₅ and at subsequent intervals of 18 min. A total of nine additions were typically made in each experiment. This procedure allowed a depletion for 3-methylfuran of 81% and a depletion for the reference compound of 72% to be achieved. In FTIR experiments only one addition of N₂O₅ at (1.1 × 10¹⁵) molecule cm⁻³ was performed. This procedure allowed a depletion for 3-methylfuran of 58–100% and a depletion for the reference compound of 59–96% to be achieved.

The initial reactant concentrations in the reactors (in molecule cm⁻³) were as follows:

- [3-methylfuran] = (2–9) × 10¹⁴
- [reference] = (1.5–9) × 10¹⁴
- [CH₃ONO]= (3–15) × 10¹⁴
- [NO]= (2-28) × 10¹⁴ and [benzene] = (4–15) × 10¹⁴

2.2. Products study

Product experiments were carried out at (298 ± 2) K and at atmospheric pressure of air in different reaction chambers: (a) in a 150 L evacuable Teflon-coated chamber equipped with six 360 nm lamps and four 254 nm lamps and with provision for sampling onto a 30/50 µm SPME (DVB/CAR/PDMS) fibre. The fibre adsorption and desorption time was 15 min at 270 ºC in split/splitless mode for the GC injection port. The analysis in this case was carried out using GC/MS and GC/FID. Products were separated in the capillary column by applying the following temperature program: from 40 ºC (4 min) to 120 ºC (12 min) at a rate of 25 ºC min⁻¹, then at a rate of 10 ºC min⁻¹ up to 200 ºC (10 min). Mass spectrometry detection was performed in electron impact mode with a detector temperature of 230 ºC. These experimental systems were used for the reactions of 3-methylfuran with OH and NO₃ radicals and Cl atoms; (b) in a 50 L Pyrex glass cell equipped with eight actinic fluorescent lamps (λ_max = 360 nm) with in situ FTIR analysis for OH and NO₃ radicals; and (c) in a 1080 L quartz-glass reactor equipped with 10 low-pressure mercury lamps (λ_max = 254 nm) and 10 superactinic fluorescence lamps (λ_max = 360 nm) coupled with in situ FTIR analysis for Cl atoms. Details of this experimental set-up can be found elsewhere (Barnes et al. 1994).

In the quantitative analysis carried out by GC/FID, the response factor (RF) of each compound was determined by introducing different measured amounts of authentic
standards (which covered the range of experimental conditions) into the Teflon chamber and conducting several replicate analyses with the coated SPME fibre. For compounds that were not commercially available or the synthesis yield of the pure compound was not sufficient to carry out the calibration, only an estimation of yield was possible using the ECN (effective carbon number) method (Scalon and Willis, 1985). The response factor of each compound was calculated with the expression:

Area = RF × [product]  

where the area is quantified from the GC/FID chromatogram and the concentration of the product is known. Sampling was performed with SMPE at the same conditions as used for the product identification experiments but the absorption time was 15 min.

In the FTIR analysis a spectral subtraction procedure was used to derive the concentrations of 3-methylfuran and products as a function of the reaction time. Identification and quantification of 3-methylfuran and products in the case of Cl reactions was carried out using calibrated reference spectra. The calibrated spectra were either produced by introducing a known concentration of an authentic sample of the compound into the reactor or were taken from an existing IR spectral library bank. Yields were calculated by plotting the amounts of product formed at each time t against the amounts of 3-methylfuran consumed at each time t.

2.2.1. Cl products

Different techniques were used to identify and quantify the reaction products at (298 ± 2) K and atmospheric pressure. The experiments involving SPME GC/MS and GC/FID/ECD techniques were conducted in ≈150 L Teflon bag placed inside a chamber with four 254 nm blacklamps. Photolysis of thionyl chloride (SOCl₂) or trichloroacetyl chloride (CCl₃COCl) was used to generate atomic chlorine in irradiation steps of 8 to 10 seconds for SOCl₂ and 10 to 60 s for CCl₃COCl. The total photolysis time was 30–90 s for SOCl₂ and 22–720 s for CCl₃COCl with a conversion of 3-methylfuran between 21 and 94%. Cl₂ was not used as the source of Cl atoms because Cl₂ reacts with 3-methylfuran at the concentration used for this study. All experiments were carried out in the absence of NO and only one qualitative experiment was carried out in the presence of NO. The initial concentrations of the reactants in the qualitative analysis (in molecule cm⁻³ units) were: [3-methylfuran] = (4.9–29) × 10¹³, [CCl₃COCl] = (1.4–2.4) × 10¹⁴,
$[\text{SOCl}_2] = (4.4–19) \times 10^{13}$ and $[\text{NO}] = 3.4 \times 10^{13}$. Electron impact (EI) and chemical ionization (CI with methane as the ionization gas) modes were used in mass spectrometry detection in order to identify and obtain molecular weight information on the different reaction products. In addition, an electron capture detector (ECD) was used to identify some reaction products. The quantitative analysis was performed in the GC/FID using SOCl$_2$ as the Cl source. The concentrations used were $(7.3–14) \times 10^{13}$ and $(7.3–15) \times 10^{13}$ molecule cm$^{-3}$ for 3-methylfuran and SOCl$_2$, respectively. The total photolysis time was 60–100 s in order to achieve a conversion of 3-methylfuran of 60–90%.

In FTIR experiments a cylindrical quartz-glass reactor of 1080 L was used. Cl atoms were generated by the photolysis of ClCOCOCl and Cl$_2$ using 10 low-pressure mercury lamps and 8 superactinic fluorescence lamps, respectively. The total photolysis time was 11–25 min for ClCOCOCl and 23 min for Cl$_2$ and under these conditions the 3-methylfuran conversion was 33–95%. The reactions between 3-methylfuran and Cl$_2$ were found to be negligible in the quartz-glass reactor under the conditions used. The use of molecular chlorine as the source of Cl atoms therefore avoided potential photolysis at 254 nm of the products generated in the reaction.

The initial concentrations of the reactants (in molecule cm$^{-3}$ units) were: $[\text{3-methylfuran}] = (1.9–2.9) \times 10^{13}$, $[\text{Cl}_2] = (4.9–7.3) \times 10^{13}$ and $[\text{ClCOCOCl}] = 1.2 \times 10^{13}$. The reactants were injected directly into the reaction chamber using calibrated gas-tight syringes through an inlet port located on one of the chamber end flanges and the chamber was pressurised to 1 atm total pressure with air. The reactant 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 an FTIR spectrophotometer (Thermo Nicolet Nexus) equipped with a KBr beam splitter and MCT detector. The IR spectra were recorded in the 700–4000 cm$^{-1}$ spectral range with 1 cm$^{-1}$ resolution by co-adding 64 interferograms over 60 s. In typical experiments 25 spectra were recorded over a period of 25 min with light.

### 2.2.2. OH products

The qualitative determination of products was carried out using GC/MS and FTIR analysis and quantitative determination was performed using GC/FID (Acme 6100 GC Young). Two OH precursors were used in the products studies by GC/MS in order to
study the influence of NO\textsubscript{x} on the reaction mechanisms: H\textsubscript{2}O\textsubscript{2} photolysed from 60 seconds to 60 minutes with the 254 nm lamps and CH\textsubscript{3}ONO in the presence of NO photolysed from 20 to 30 seconds with the 360 nm lamps. After every photolysis a chromatogram was recorded and total photolysis times of 150–180 s and 106 min for CH\textsubscript{3}ONO and H\textsubscript{2}O\textsubscript{2} were attained, respectively, to achieve 75–99\% depletion of 3-methylfuran in the first case and 36\% depletion in the second case. The initial reactant concentrations in the chamber (in molecule cm\textsuperscript{-3}) were as follows: [CH\textsubscript{3}ONO] = (1.3–2.1) \times 10^{14}, [NO] = (3.2–4.4) \times 10^{13}, [3-methylfuran] = (3.6–12) \times 10^{13} and [H\textsubscript{2}O\textsubscript{2}] = 2.8 \times 10^{14}. In the quantitative analysis only CH\textsubscript{3}ONO was used as the OH source.

In FTIR product experiments only CH\textsubscript{3}ONO was used as a precursor and this was photolysed continuously with eight 360 nm lamps resulting in a conversion of 3-methylfuran of up to 70\%. The FTIR system used was the same as that described for the kinetic studies. The initial concentrations in the cell (in molecule cm\textsuperscript{-3}) were: [CH\textsubscript{3}ONO] = 2.6 \times 10^{14}, [NO] = 2.6 \times 10^{14} and [3-methylfuran] = 2.6 \times 10^{14}.

### 2.2.3. NO\textsubscript{3} products

Only a qualitative analysis was carried out due to the absence of commercially available nitrated standards. The identification of products was performed using GC/MS and FTIR. In the GC/MS experiments the initial concentration of 3-methylfuran in the chamber (in molecule cm\textsuperscript{-3}) was 4.7 \times 10^{13}. Successive additions of N\textsubscript{2}O\textsubscript{5} were performed corresponding to a final concentration of 2.4 \times 10^{13} molecule cm\textsuperscript{-3}, which resulted in an approximately 95\% depletion of 3-methylfuran. In the case of FTIR the initial concentrations in the reactor (in molecule cm\textsuperscript{-3}) were: [N\textsubscript{2}O\textsubscript{5}] = (2.8–2.9) \times 10^{14} and [3-methylfuran] = (2.4–2.9) \times 10^{14} to achieve a 17\% conversion of 3-methylfuran.

### 2.2.4. Chemicals

The chemicals used and their stated purities were as follows: 3-methylfuran (Acros, 98\%), 5-methylfurfural (Aldrich, 99\%), 3-furaldehyde (Aldrich, +97\%), \(\alpha\)-pinene (Fluka, 99\%), 3-methyl-2,5-furanodione (Acros, 98\%), 3-methyl-2(5H)-furanone (Aldrich, 90\%), 5-hydroxy-4-methyl-2(5H)-furanone (Ochem, 97\%), crotonaldehyde (Aldrich, 99\%), acetic acid (Aldrich, +99.99\%), 2-methylpropenoic acid (Aldrich, 99\%), 2-butenoic acid (Aldrich, 98\%), SOCl\textsubscript{2} (Aldrich, +99\%), CCl\textsubscript{3}COCl (Aldrich, 99\%) and CICOCOCI (Aldrich, 98\%). Gaseous products: \textit{trans}-2-butene (Aldrich,
The following compounds were used in methyl nitrite synthesis: NaNO₂ (Panreac, 97%), H₂SO₄ (Panreac, 95–98%) and CaCO₃ (Riedel-de-Haën AG, 99%). In N₂O₅ synthesis: N₂O₄ (Fluka, >98.5%) and O₂ (Praxair, 99.999%). Hydroxymethyl-2(5H)-furanones [5-hydroxy-3-methyl-(5H)-furanone and 5-hydroxy-4-methyl-2(5H)-furanone] were prepared from 3-methylfuran according to Kumar and Pandey (2000). The product was characterised by GC-MS.

3. Results and discussion

3.1. Kinetic studies

In agreement with the equations (1) and (2), the data yield straight lines that pass through the origin with a slope of \( k_S/k_R \) indicating that secondary reactions or heterogeneous processes are insignificant (See Figure 1 and 2 of supporting information). The error limit for the ratio of rate coefficients \( k_S/k_R \) includes only the precision of the fit to our experimental data (±2\( \sigma \)). The \( k_S \) error limit, \( \sigma_{k_S} \), has been calculated taking into account the error limit from the slopes obtained from the regression analysis and the quoted error in the value of the rate coefficient for the reference compound.

The weighted mean \( k_S \) values and the rate coefficient ratios \( k_S/k_R \) obtained from least-squares analyses using GC/FID and FTIR techniques are given in Table 1. The data show that within error there is no significant difference between runs by GC/FID/MS or FTIR. As can be seen from the results in Table 1, the high values of the OH rate coefficients (in the order of \( 10^{-10} \) cm³ molecule⁻¹ s⁻¹) show the high reactivity of OH radicals towards 3-methylfuran. Available literature data are also shown in Table 1. It can be observed that the weighted mean rate coefficient data for the reaction of 3-methylfuran with OH are slightly higher than the literature data (Atkinson et al., 1989) but these can be considered similar due to experimental errors. The rate coefficients for OH reactions can be estimated by the AOPWIM program from the SAR method (Aschmann and Atkinson, 1995). The value of rate constant for 3-methylfuran and OH calculated in this way is \( 1.05 \times 10^{-10} \) cm³ molecule⁻¹ s⁻¹, which is similar to the average rate coefficient value obtained in this work.
In relation to reaction of 3-methylfuran with NO\textsubscript{3}, the rate constant obtained in this work is consistent with the data obtained by Alvarado et al. \cite{1996}. Therefore a mean value between the rate constants for OH and NO\textsubscript{3} radicals determined in this study and the ones obtained by Atkinson et al. \cite{1989} and Alvarado et al. \cite{1996} respectively can be proposed as good reference data.

According to the rate coefficients reported in Table 1 for the reaction of 3-methylfuran with OH and NO\textsubscript{3} radicals, together with data for Cl atoms reported in our previous work \cite{2005}, it can be established the following order of reactivity: \(k_{\text{Cl}} > k_{\text{OH}} > k_{\text{NO}_3}\). In addition in Cabañas et al. \cite{2005} a comparative study of the rate constants with available literature values for mono and dimethylated furans was reported.

### 3.2. Products studies

The major challenge in identifying the reaction products from the reaction of 3-methylfuran with OH, NO\textsubscript{3} radicals and Cl atoms is the scarcity of commercially available standards. The identification of reaction products was carried out using the custom GC-MS and FTIR libraries created after the injection of commercial products [3-furaldehyde, 3-methyl-2,5-furanodione, 3-methyl-2(5\textsubscript{H})-furanone, 5-hydroxy-4-methyl-2(5\textsubscript{H})-furanone, crotonaldehyde, acetic acid, 2-methyl-propenoic acid and 2-butenoic acid], or compounds synthesized in our laboratory [2-methylbutenedial, 5-hydroxy-3-methyl-(5\textsubscript{H})-furanone and 5-hydroxy-4-methyl-2(5\textsubscript{H})-furanone] or using commercial GC-MS library (NIST 21, NIST 27, NIST 107, NIST 147 and WILEY 229) and Aldrich Library FTIR spectra \cite{1989}. The results are explained in detail below for each reaction.

#### 3.2.1. Reaction with Cl atoms

An example of a typical chromatogram is shown in Figure 1A for the oxidation of 3-methylfuran by Cl atoms in the absence of NO at different reaction times and in the presence of NO (upper chromatogram). Peaks A and C represent artefact compounds from the chlorine source and from the fibre, respectively. 3-Methylfuran is represented by peak B. The only compounds identified by the mass spectra and by the retention times of authentic standards are 3-furaldehyde (peak D), 3-methyl-2,5-furanodione (peak H) and 3-methyl-2(3\textsubscript{H})-furanone (peak I). Analysis of the EI mass spectrum of peak E shows the presence of the compound C\textsubscript{5}H\textsubscript{6}O\textsubscript{2} and the chemical ionization (CI)
mass spectrum of this peak shows that its molecular weight is 98. This peak can therefore be tentatively assigned to an isomer of 3-methyl-2(3H)-furanone or 2-methylbutenedial. Peaks F and G are assigned to \((E/Z)-2\text{-methylbutenedial}\) based on the EI fragmentation and by comparison of the mass spectrum with the reference mass spectrum and the retention time of the synthesized compound. Peaks L and M are assigned to 5-hydroxy-3-methyl-2(5H)-furanone and 5-hydroxy-4-methyl-2(5H)-furanone, respectively, based on EI fragmentations and the CI mass spectra, which indicate that the molecular weight is 114 (see Figure 3 in supporting information). The synthesis of the isomers of hydroxy-methylfuranones confirmed the presence of these compounds by comparison with the mass spectra and retention times. Furthermore, comparison with the commercial 5-hydroxy-4-methyl-2(5H)-furanone confirmed that this compound gave rise to peak M. Peaks J and K – with retention times of 20.9 and 23.9 min, respectively – are the most intense and were identified as chlorinated organic compounds of molecular formula \(C_5H_5O_2\)Cl based on the following evidence: (a) the CI mass spectrum shows that the molecular ion is at \(m/z\) 132, (b) the fragmentation pattern from the electron impact mass spectrum is also consistent with this compound and (c) the gas chromatogram obtained with electron capture detection (ECD), which is particularly sensitive to chlorinated compounds, shows only two intense peaks at 20.9 and 23.9 min. Additionally, in previous experiments 5-chloro-2(5H)-furanone was detected as a product from the reactions of furan (Villanueva et al., 2007), 2-methylfuran and 2-ethylfuran (Villanueva et al., 2009) with Cl atoms, therefore it is believed that peaks J and K could be assigned to chlorinated methylfuranones [5-chloro-3-methyl-2(5H)-furanone and 5-chloro-4-methyl-2(5H)-furanone]. Peaks J and K could also be assigned to acid chlorides (3-methyl-4-oxo-2-butenoyl chloride or 2-methyl-4-oxo-2-butenoyl chloride) \([\text{HOC–CH=CH(CH}_3\text{)–COOH}]\) in the same way as 4-oxo-2-pentenoyl chloride was identified in the reaction of 2-methylfuran with Cl atoms. Both chlorinated methylfuranones and acid chlorides could be formed by the addition of Cl to the two ortho positions. The EI and CI mass spectra of peaks J and K are shown in Figure 4 (in supporting information). The molecular ion peak in the CI mass spectrum (MW 132) shows a fragment from a more stable ion \([M + 1 – 34 = 99\text{ da}]\). As described below for the FTIR analysis, the chlorinated methylfuranones are probably the compounds that are formed to the greatest extent. As shown in Figure 1A the reaction
products in the absence and in the presence of NO are similar. The only difference probably concerns the yields.

The yields of some compounds were estimated using the response factors of structurally related and commercially available compounds (i.e. the ECN method). The response factor for 2-methylbutenedial, its isomer (peak E) and chlorinated methylfuranones were estimated by taking into account the response factor of 3-methyl-2(5H)-furanone.

The concentration-time dependency for the reaction products identified in the reaction of 3-methylfuran with Cl (see Figure 2) provides information about the secondary reactions that the products undergo. A slight curvature downwards could suggest the loss of some reaction products by deposition on the walls, photolysis or reaction with Cl atoms. The concentrations of the reaction products were calculated using the mathematical formalism of Tuazon et al. (1986), where the loss processes such as photolysis and wall loss have been taken into account. For 3-furaldehyde the reaction with the Cl atom was also considered using the rate coefficient obtained by Cabañas et al. (2008). The curve contours for chlorinated methylfuranones, 3-furaldehyde and 2-methylbutenedial indicate that these are primary products while the rest of products are probably secondary. A quantitative analysis in the presence of NO was not performed due to the occurrence of secondary reactions that involve the formation of OH in the reaction system (Wang et al., 2005).

FTIR spectra recorded for different stages of the reaction of 3-methylfuran with Cl are shown in Figure 3A: (a) spectrum of 3-methylfuran+Cl₂ in air before photolysis, (b) spectrum of 3-methylfuran and products after 15 min of photolysis (absorptions from CO₂ have been zeroed due to saturation of the band and those from H₂O have been subtracted), and (c) the residual product spectrum after subtraction of 3-methylfuran. The residual spectrum of the products shows the presence of HCl and CO, a band with a high intensity at 1825 cm⁻¹, bands of medium intensity in the region 800–1300 cm⁻¹ and two bands of low intensity in the carbonyl region at 1710 and 1665 cm⁻¹. Based on the results obtained by SPME-GC/MS the band at 1710 cm⁻¹ is assigned to 3-furaldehyde – an assignment also based on a comparison with the reference spectrum. The bands at 1703 and 1665 cm⁻¹ can be tentatively assigned to 2-methylbutenedial, but due to the low purity of the 2-methylbutenedial synthesized this can not be confirmed from the IR spectrum. Based on the GC/MS results and those obtained in our previous studies on the reaction of Cl atoms with furan (Villanueva et al., 2007), 2-methylfuran and 2-
ethylfuran (Villanueva et al., 2009), the band at 1825 cm$^{-1}$ can be assigned to the chlorinated methylfuranone isomers 5-chloro-3-methyl-2(5$H$)-furanone and 5-chloro-4-methyl-2(5$H$)-furanone. The band at 1825 cm$^{-1}$ is very similar in appearance to that observed in our previous studies for the reaction of Cl atoms with alkylfurans, where the band at 1829 cm$^{-1}$ was assigned to 5-chloro-2(5$H$)-furanone and confirmed by comparison with the reference spectrum of a synthesized sample. The possibility that the compound was an acid chloride (3-methyl-4-oxo-2-butenoyl chloride or 2-methyl-4-oxo-2-butenoyl chloride) was ruled out as the infrared spectrum is devoid of any absorption bands in the region 2695–2900 cm$^{-1}$, which would be characteristic for the stretching vibration of C–H in the –CHO group.

The gas-phase IR absorption coefficients for chlorinated methylfuranones are not known. As a consequence, the concentrations of these compounds were estimated by applying the Beer-Lambert Law for the absorption band at 1825 cm$^{-1}$ using the known absorption coefficient for the structurally related compound 2(5$H$)-furanone, which was measured using the 1080 L chamber. The calculated yield of chlorinated methylfuranones is the sum of the concentrations of the two isomers as the IR spectrum is a mixture of the two individual ones. The yield of CO was not calculated because it is a secondary product that only appears at the end of the reaction.

The product yields were calculated from the slopes of plots of products formed versus 3-methylfuran reacted; it should be noted that on using UV lamps the secondary reactions are almost negligible in the early stages of the reaction (Bierbach et al. 1995). The molar yields obtained for the products identified by SPME/GC-FID and FTIR are given in Table 2 together with their retention times, molecular weights. The total error is a combination of statistical error 2σ obtained in regression analysis and uncertainties estimated in the calibrations. Although it was not possible to quantify all of the identified compounds, if we compare the results from the quantification methods, SPME-GC/FID and FTIR, it is clear that chlorinated methylfuranones are the major gas-phase reaction products of the reaction between Cl atoms and 3-methylfuran. Despite the overall uncertainties associated with each quantification method, the yields of the products are in fair quantitative agreement. A total carbon mass balance of 70% was obtained for the products detected in GC-FID experiments and 90% for the products determined by FTIR. These values must be treated with caution because the yield of chlorinated methylfuranones could be underestimated by GC-FID, as occurred in the
case of the chlorinated furanone formed from furan and alkylfurans with Cl atoms or overestimated in the case of FTIR (Villanueva et al., 2007, 2009).

3.2.2. Reaction with OH radicals

An example of a typical chromatogram of the oxidation of 3-methylfuran by OH radicals in the presence of NO is shown in Figure 1B. 3-Methylfuran is represented by peak A. The only compounds identified by the mass spectrum and by the retention time of authentic standards are acetic acid (peak B), 3-furaldehyde (peak C), 2-methylbutenedial (peak E), 3-methyl-2,5-furanodione (peak F), 3-methyl-2(3H)-furanone (peak G) and 5-hydroxy-4-methyl-2(5H)-furanone (peak I). Peak H is assigned to 5-hydroxy-3-methyl-2(5H)-furanone by comparison with the mass spectrum and retention time of the synthesized compound. Analysis of the EI mass spectrum of peak D shows the presence of a compound of formula C5H6O2 but this was not assigned to any particular structure.

The concentrations of the reaction products were calculated with the response factors determined using the procedure outlined in the Experimental Section and as indicated in the reactions of Cl atoms for the common products. The yields (%C) of the primary products 2-methylbutenedial (1.4 ± 0.3) and 3-furaldehyde (3.9 ± 1.8) and the secondary products 3-methyl-2,5-furandione (18.1 ± 4.6) and 3-methyl-2(3H)-furanone (1.6 ± 0.2) were obtained from the slopes of plots of the concentration of reaction product formed versus the amount of 3-methylfuran consumed.

The qualitative SPME-GC/MS analysis carried out using H2O2 as a clean source of OH shows the same peaks as those obtained using methylnitrite along with five new peaks that are very weak; three of the new peaks were identified as being due to crotonaldehyde, 2-methylpropenoic acid and 2-butenoic acid by their mass spectra and retention times of authentic samples. Two peaks at 22.4 and 22.8 min were identified from the spectra library as 4-methyl-2(5H)-furanone and methylsuccinic anhydride, but it is a tentative identification because they were not compared with commercial standards.

In the case of FTIR experiments, and due to low signal intensity, the reaction products were only tentatively assigned in order to complete or confirm the results from SPME/GC-MS. The residual FTIR spectrum for the product obtained in the oxidation of 3-methylfuran with OH radicals in the presence of NO is shown in Figure 3B after subtraction of the spectra of 3-methylfuran, NO2, NO, HCHO, HNO3, HONO and
CH3ONO. Only 3-methyl-2,5-furanodione was identified by comparison with the bands of an authentic standard (898, 1792 and 1858 cm$^{-1}$). Although 2-methylbutenedial was identified by GC-MS analysis, identification by FTIR was not possible due to the low purity of the synthesized compound. Thus, the band at 1711 cm$^{-1}$ in Figure 3B was assigned to 2-methylbutenedial by comparison with the bands of other 1,4-dicarbonyl compounds such as butenedial and based on the results obtained in the GC-MS.

2-methylbutenedial, was identified and quantified (yield of (83 ± 33)%) as major reaction product by Gómez Álvarez et al. (2009) in the study of the degradation of 3-methylfuran with OH radicals. The low yield (1.4%) obtained in our work could be due to the occurrence of secondary reactions to form products such as 3-methyl-2(3H)-furanone and 3-methyl-2,5-furanodione. The secondary reactions that imply the loss of 2-methylbutenedial (photolysis process, reaction with OH radical, wall loss, etc) is supported by several facts: 1)- Bierbach et al. (1995) reported that the yield of 4-oxo-2-pentenal (unsaturated 1,4-dicarbonyl) in the reaction of 2-methylfuran with OH radiacal varied from ≈70% at the beginning of the reaction to ≈47% at the end. Due to photolysis of the compound and probably to the oxidation of the dicarbonyl compound with OH radicals (Bierbach et al., 1994, Tang and Zhu, 2005). 2) -the decay in the intensity of the band at 1711 cm$^{-1}$ with the time in our experiments. From analysis of the decay of this band (supposing a decay of first order) a rate constant of 0.026 s$^{-1}$ can be estimated what means a very fast loss process. In the next section a possible sequence of reactions that 2-methylbutenedial can suffer is commented. The reason why secondary reactions take place in a higher extension in our experiments than in Bierbach et al. (1995) and Gómez Álvarez et al. (2009) could be due to the different experimental conditions used.

The bands at 795, 1297 and 1734 cm$^{-1}$ are typical of nitroperoxy compounds (ROONO$_2$) formed from the reaction of peroxy radicals with NO$_2$ (Wängberg et al. 1997, Martín et al. 2002). One of the most intense bands is observed at 1820 cm$^{-1}$ that can be assigned to a carbonyl group that together with the band of 1014 cm$^{-1}$ typical of OH group support such as that in the hydroxy-methylfuranones. This assignment is supported from the displacement that the wavelength of the -CO group suffers to higher values due to the presence of a -OH group with a positive conjugative effect (+K) in β position. For example in the 5-ethyl-2-tetrahydrofuranone the band of –CO appears at 1811 cm$^{-1}$ while in the 5-hydroxymethyl-2-tetrahydrofuranone this band appears at
1823 cm$^{-1}$ due to the positive conjugative effect of the –OH group. On the other hand
the band at 1014 cm$^{-1}$ can be due to a –OH group in β position in relation to a -CO
group. It is known that groups with a negative conjugative effect (-K) next to a -OH
groups cause the displacement of the band to lower values. For example, C-OH
absorption band of 3-hydroxyfuran appears at 1087 cm$^{-1}$ and in 4,4-dimethyl-3-
hydroxy-2-furanone appears at 1015 cm$^{-1}$. However, hydroxy-methylfuranones was not
confirmed due to the low purity of the commercial compound. In the reaction of 2-
methylfuran with OH radicals Bierbach et al. (1995) observed a band at 1820 cm$^{-1}$ that
was not assigned. Furthermore, Gómez Álvarez et al. (2009), in the reaction of 3-
methylfuran with OH radicals (but in the aerosol phase), obtained a compound with a
molecular weight of 114, which was tentatively assigned to 4-keto-pentenoic acid based
on the molecular formula C5O3H6. This molecular formula also corresponds with 5-
hydroxy-2(5H)-methylfuranone. Based on the intensities of the peaks obtained by GC/MS, and taking into account that
only 24% of the reacted carbon was identified, it is likely that the bands at 1820 cm$^{-1}$
and 1014 cm$^{-1}$ are due to the isomers identified by GC/MS. Compounds such as CO
(2115 and 2176 cm$^{-1}$) and CO$_2$ (2360 cm$^{-1}$) are also evident and the intensity of their
bands increase with time, which signifies that open compounds could be forming during
the reaction.

### 3.2.3. Reaction with NO$_3$ radicals

An example of a typical chromatogram from the oxidation of 3-methylfuran by NO$_3$
radicals is shown in Figure 1C. 3-Methylfuran is represented by peak A. The following
compounds were identified by their mass spectra and the retention times of authentic
standards: (Z/E)-2-methylbutenedial (peaks D and E), 3-methyl-2,5-furanodione (peak
F), 3-methyl-2(3H)-furanone (peak G) and 5-hydroxy-4-methyl-2(5H)-furanone (peak
J). It is known that nitrated compounds should be present as products from the reaction
of 3-methylfuran with NO$_3$ radicals but due to the sampling method and analysis
conditions (very high temperature in the injection port) these compounds were not
identified by the SPME-GC/MS technique.

The residual product FTIR spectrum from the oxidation of 3-methylfuran with NO$_3$
radicals after subtraction of the spectra of 3-methylfuran, N$_2$O$_5$, NO$_2$ and HNO$_3$ is
shown in Figure 3C. The bands at 792, 1294 and 1732 cm$^{-1}$ are assigned to nitroperoxy
compounds (–OONO$_2$) based on the fact that nitroperoxy compounds decompose with
time (Hjorth et al., 1990; Wängberg and Ljungström, 1992) what was confirmed experimentally.

The bands at 857, 1287, 1660 and 1695 cm\(^{-1}\) are assigned to nitrooxy compounds (–ONO\(_2\)) considering that the typical bands of this group appear at 843, 1296 and 1672 cm\(^{-1}\) (Tuazon et al., 1999). In our case appear two bands around at 1672 cm\(^{-1}\) (1695 and 1660 cm\(^{-1}\)). These bands can be explained by the presence of two reaction products. One product with a hydroxyl group and a –ONO\(_2\) group, and other product with a carbonyl group a –ONO\(_2\) group. So, the presence of an OH group, with positive conjugative effect (+K), would shift the –ONO\(_2\) absorption band to a higher wavenumber of 1672 cm\(^{-1}\) such as the band at 1695 cm\(^{-1}\), likewise a CO group with negative conjugative effect (–K) would shift the –ONO\(_2\) absorption band to a lower wavenumber of 1672 cm\(^{-1}\) such as the band at 1660 cm\(^{-1}\). On the other hand the presence of the bands at 1061 and 1090 cm\(^{-1}\) confirm the presence of hydroxynitrate compounds where the nitrate group displaces the C–OH band to higher wavenumber by the same positive conjugative effect. In the next section scheme 5 shows the reaction mechanisms for the formation these compounds. The simultaneous presence of these two sets of bands (792, 1294, 1732 and 857, 1287, 1660, 1695 cm\(^{-1}\)) can also suggest the formation of R(ONO\(_2\))(OONO\(_2\))-type compounds (Martín et al., 2002).

The bands at 1829–1835 cm\(^{-1}\) can be assigned to the carbonyl group of the lactone with a –ONO\(_2\) group in β position. The effect of –ONO\(_2\) group on the carbonyl band in the lactone produce a similar displacement (to higher wavenumber) to that produced by Cl in chlorinated methylfuranones (Villanueva et al. 2007). On the other hand, Wängberg et al. (1997) associated the band found at 1829 cm\(^{-1}\) with an acetyl peroxynitrate group [–C(O)O\(_2\)NO\(_2\)] after the reaction of pinonaldehyde with NO\(_3\). In conclusion, based on the results obtained with Cl and OH, the band at 1829 cm\(^{-1}\) together with the bands at 857, 1287, 1660 could be assigned to the isomers of nitrooxy-methyl-2(5H)-furanone (see scheme 5).

The band at 1021 cm\(^{-1}\) can be due to a C–OH group of the hydroxyfuranone compounds, where the carbonyl group has a negative conjugative effect and displaces the C–OH band to lower wavenumber. This band together with the absorption at 820 cm\(^{-1}\), also can be also assigned to a C-O bond stretch and ring vibration of an epoxy group (Pounchert, 1989). These absorptions decreased markedly with time indicating that the possible epoxy compound formed in the reaction is thermally unstable. The
epoxy compound has been observed in others studies of NO₃ radical (Wångberg et al., 1997, Martín et al., 2002).

Compounds such as 3-methyl-2,5-furanodione, 3-methyl-2(3H)-furanone and 5-hydroxy-4-methyl-2(5H)-furanone were not found in the FTIR analysis, probably because the bands were overlapped by the bands of the major products.

4. Reactions mechanism

From the literature data on the reactivity of compounds with double bonds and heteroatoms in their structure, e.g. allyl acetate, propyl vinyl ether, 2-methyl-2-butenal and crotonaldehyde, it is known that these compounds undergo addition processes to the double bonds and abstraction of different H atoms in the presence of OH, generating primary and secondary carbonyl products (Magneron et al., 2002; Picquet-Varrault et al. 2002; Tuazon et al., 2005; Zhou et al., 2006). Based on previous studies it is known that the reaction of NO₃ radicals with open and cyclic alkenes begins with the addition of the radical to the double bond, while the H-atom abstraction does not occur at all (Barnes et al., 1990; Hjorth et al., 1990; Skov et al., 1992; Jones and Ham, 2008; Rollins et al., 2009). This implies that the main products for the reaction of 3-methylfuran with OH radicals, NO₃ radicals and Cl atoms will come from the addition of the radical or atom to positions C2 or C5 because the most stabilized reaction intermediates are generated. H-atom abstraction is also likely to occur but this will only be a minor process. So, based on literature data, our previous work Villanueva et al. (2007, 2009) and the products indentified in this work different reaction pathways for the reaction of 3-methylfuran with Cl, OH and NO₃ have been proposed. Schemes 1–6.

In the scheme 1 the process for the generation of 2-methylbutenedial in the reaction of 3-methylfuran with OH, NO₃ and Cl atoms is shown. 2-Methylbutenedial is a primary product that arises from the addition of the oxidant to a double bond in the C2 or C5 position, with the intermediate undergoing ring opening and, depending on the nature of the substituent X (X: OH, NO₃, Cl), the process will be different. For the reaction with OH, the O₂ abstracts the H-atom whereas in the case of Cl atoms and NO₃ radical the good characteristics of Cl and NO₂ as leaving groups mean that these groups are eliminated. This mechanism is also proposed by Bierbach et al. (1995) and Berndt et al. (1997).
The process for the generation of 3-methyl-2(3H)-furanone in the intramolecular photoisomerization of 2-methylbutenedial in the presence of VIS and UV radiation is represented in Scheme 2 (Bierbach et al., 1994). In the case where X is NO$_3$ there is no radiation but the presence of HNO$_3$ probably stabilizes the zwitterionic intermediate and thus favours the process. Bierbach et al. (1994) proposed possible reaction pathways for the formation of maleic anhydride from the OH-initiated degradation of butenedial and 4-oxo-2-pentenal. Likewise, it is possible to propose a mechanism for the formation of 3-methyl-2,5-furanodione from the abstraction of the aldehydic hydrogen of 2-methylbutenedial (see Scheme 3). In this case 3-methyl-2,5-furanodione would be a secondary product whose yield, together with the yield of 3-methyl-2(3H)-furanone, would give us the molar yield of 2-methylbutenedial. In the reaction of 3-methylfuran with OH radicals the yield of 3-methyl-2,5-furanodione is high (18%) and this indicates that 2-methylbutenedial would be a main product.

A possible reaction pathway for the formation of 3-furaldehyde in the reaction of 3-methylfuran with OH, NO$_3$ and Cl as the primary product is represented in Scheme 4. Although the abstraction of an H-atom from a methyl group is not favoured according to the literature, it is known that benzaldehyde is a major product in the reaction of Cl with toluene (Wang et al., 2005; Nozière et al., 1994). However, base on the yield obtained in this study (where the higher yield is about 7% for Cl reaction) this process is not as favoured as addition.

In Scheme 5 a global reaction sequence for the reaction of 3-methylfuran and X radicals (OH, NO$_3$ or Cl) has been proposed. The sequence is initiated by the addition of radical X to the carbon-carbon double bond at the 2- and/or 5-positions. In the case of the NO$_3$ radical the resulting nitrooxyalkyl radicals can either decompose to the epoxide (compounds A and/or A’) plus NO$_2$ (this process typically decreases in importance as the total pressure and O$_2$ content increases) or add O$_2$ to form nitrooxyalkyl peroxy radicals (5-ONO$_2$-3-methylfuran peroxyradical or 5-ONO$_2$-4-methylfuran peroxyradical) (Atkinson, 1991; Atkinson, 1997). The nitrooxyalkyl peroxy radicals can (a) react with NO$_2$ to form thermally unstable peroxydinitrates [R(ONO$_2$)(OONO$_2$) compounds B and/or B’], (b) react with HO$_2$ radicals to form nitrooxy hydroperoxides (compounds C and/or C’) and (c) react with organic peroxy (RO$_2$) radicals. The reactions with organic peroxy radicals (including the self-reaction) proceed through a “molecular” channel, forming a nitrooxy alcohol and/or (if feasible) a nitrooxy carbonyl
compound (compounds D and E and/or D’ and E’), and through a “radical” channel to form the nitrooxy alkoxy radicals (5-ONO$_2$-3-methylfuran alkoxyradical or 5-ONO$_2$-4-methylfuran alkoxyradical). The latter radicals are expected to (a) decompose to form dicarbonyl compounds as products (compounds F and/or F’), (b) add NO$_2$ to form dinitrate compounds [R(ONO$_2$)$_2$(ONO$_2$) compounds G and/or G’] or (c) add molecular oxygen to form nitrooxycarbonyl compounds [compounds E and/or E’, 5-nitrooxy-2(5H)-methylfuranone] plus the HO$_2$ radical. Our FT-IR results are consistent with Scheme 5, with evidence for the formation of the epoxide (band 820 cm$^{-1}$ compound A or A’), nitrooxy alcohol (compound D or D’) and nitrooxy carbonyl (compounds E or E’). The same sequence of reactions could be initiated by OH and Cl radicals and the products formed would be the same on changing X (ONO$_2$) for Cl or OH. Compounds E and E’ would therefore be 5-chloro-2-(5H)-methylfuranones for the reaction of 3-methylfuran with Cl atoms and 5-hydroxy-2(5H)-methylfuranones for the reaction with OH radicals. However, in the reaction with Cl atoms and OH radical there was no evidence in the product analysis for the formation of compounds D/D’.

In conclusion the addition process with retaining configuration is the most important pathway for the reaction of 3-methylfuran with Cl atoms. This fact is corroborated by the high yields of 5-chloro-2(5H)-methylfuranones. In the case of the reaction with OH the dominant reaction pathway is the ring opening although it is believed that 5-hydroxy-2(5H)-methylfuranones (retaining configuration product) is a significant product although it could not be quantify. For the reaction with NO$_3$ although 5-nitrooxy-2(5H)-methylfuranones (retaining configuration products) were not identified by GC/MS and they were only tentatively assigned to certain bands in the IR spectrum, their formation is likely given the results obtained in the OH and Cl reactions. In addition, due to the low yield obtained for 2-methylbutenedial it is not possible to determine the dominant reaction pathway.

The presence of 5-hydroxy-4-methyl-2(5H)-furanone and 5-hydroxy-3-methyl-2(5H)-furanone as products in the reaction of 3-methylfuran with NO$_3$ and Cl was also confirmed. 5-Hydroxy-2(5H)-furanone was detected in the reaction of furan and alkylfurans with Cl atoms (Villanueva et al., 2007, 2009). In the case of furan, this compound was expected to be formed as a result of H-abstraction from the aromatic ring. Similarly, in the reactions of 3-methylfuran with NO$_3$ radicals and Cl atoms, 5-hydroxy-2(5H)-methylfuranones can only be generated by H-atom abstraction from the aromatic
ring in positions C2 or C5 (see Scheme 6). There are several reaction pathways for RO\(_2\) + RO\(_2\) radical reactions and one involves the formation of an alcohol (R–OH) and a carbonyl (RCO) co-product, as shown in Scheme 6. In this particular reaction scheme the carbonyl co-product formed is 3-methyl-2,5-furandione, which is observed experimentally. It was found in some studies that the abstraction of an H-atom from the aromatic ring in the reactions of p-xylene and 1,2,4-trimethylbenzene with OH is not favoured and the yields of the resulting methylquinones are low in comparison with the products obtained in the addition processes (Smith et al., 1999). In the case of the reaction of 3-methylfuran with NO\(_3\) and Cl, 3-methyl-2,5-furanodione is formed as a co-product and therefore for Cl reactions it is likely to provide a means to estimate the yield of the 5-hydroxy-2(5\(H\))-methylfuranones. Thus the yields of the 5-hydroxy-2(5\(H\))methylfuranones are expected to be ≤ 8%.

It is important to note that the degradation mechanism of 3-methylfuran with Cl atoms is the same as that proposed for furan with Cl atoms and this will yield the same products as obtained from furan but with the corresponding methyl group (Villanueva et al., 2007).

5. Atmospheric implications

The kinetic data obtained in this study can be used to calculate atmospheric lifetimes for 3-methylfuran due to reaction with the oxidants OH, NO\(_3\), Cl and O\(_3\) by applying Eq. (4)

\[ \tau_{\text{total}} = \frac{1}{k_X[X]} \]  

and the average concentrations of these compounds in the troposphere: [OH] = 1 × 10\(^6\) radicals cm\(^{-3}\) (Prinn et al., 1992), [NO\(_3\)] = 2 × 10\(^7\) radicals cm\(^{-3}\) (Finlayson-Pitts and Pitts, 2000), [Cl] = 1 × 10\(^4\) atoms cm\(^{-3}\) (Wingenter et al., 1996) and [O\(_3\)] = 7.4 × 10\(^{11}\) molecule cm\(^{-3}\) (Logan, 1985). As shown in Table 3, OH and NO\(_3\) radicals are the most important sinks for 3-methylfuran at daytime and night-time, respectively, with lifetime values of 2.5 and 1 hours.

In order to evaluate the atmospheric importance of a particular reaction it is necessary to consider the reaction mechanism and the product formation. The results of this work are consistent with the remarks and conclusions outlined below.
As explained in our previous studies (Villanueva et al., 2009), certain chlorinated compounds, such as the chlorinated-methylfuranones determined in this work, are formed in the atmosphere from the reaction of Cl atoms with the parent VOC. Therefore, if a chlorinated product can be identified from a particular reaction involving Cl, these products could serve as “markers” in the chemistry of Cl atoms in the troposphere.

On the other hand, the majority of compounds identified from the reaction of 3-methylfuran with NO$_3$ are nitrated compounds. These compounds can act as NO$_x$ reservoir species (or sinks), especially during the night.

In recent years, the California Air Resources Board (CARB) has adopted regulations for volatile organic compounds (VOCs) based on calculations of their relative ground-level ozone impacts. For the purposes of these regulations, these impact levels are quantified using the Maximum Incremental Reactivity (MIR) scale. This scale was developed by Carter (1994a) and is based on model calculations for the effects of additions of VOCs on ozone formation in one-day box model scenarios that represent conditions where ambient ozone is most sensitive to changes in VOC emissions.

These calculations require a model or models for airshed conditions, a method for quantifying ozone impacts, and a chemical mechanism to calculate the effects of the reactions of VOCs on ozone formation in the atmosphere. In the last calculation of MIR values, 3-methylfuran was included and its value is 6.9 g s$^{-1}$ (Carter, 2010). This value means that 3-methylfuran is a potential source of ozone generation to a greater extent than other compounds that are more abundant in the atmosphere due to its high atmospheric reactivity with the main atmospheric oxidants.

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Table 1. Rate coefficients for the reactions of 3-methylfuran with OH and NO₃ at atmospheric pressure and room temperature.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reference</th>
<th>$k_3/k_R^{a}$</th>
<th>$k_{298K}^{b}/10^{-10}$ cm⁻³molec⁻¹s⁻¹</th>
<th>$k_{298K}/10^{-10}$ cm⁻³molec⁻¹s⁻¹</th>
<th>Method</th>
<th>Bibliographic reference</th>
</tr>
</thead>
<tbody>
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<td>3-Methylfuran + OH</td>
<td>trans-2-Butene</td>
<td>1.11±0.09</td>
<td>0.81±0.16</td>
<td></td>
<td>loop/GC-MS</td>
<td>This work</td>
</tr>
<tr>
<td>5-Methylfurfural</td>
<td></td>
<td>2.27±0.08</td>
<td>1.16±0.06</td>
<td></td>
<td>SPME/GC-FID</td>
<td>This work</td>
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<tr>
<td>trans-2-Butene</td>
<td></td>
<td>1.24±0.08</td>
<td>0.91±0.17</td>
<td>1.1±0.2²</td>
<td>FTIR</td>
<td>This work</td>
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<tr>
<td>Propene</td>
<td></td>
<td>3.6±0.3</td>
<td>1.08±0.17</td>
<td></td>
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<td>This work</td>
</tr>
<tr>
<td>2,3-Dimethyl-2-butene</td>
<td></td>
<td>-</td>
<td>-</td>
<td>0.9±0.2</td>
<td>FTIR</td>
<td>Atkinson et al., 1989</td>
</tr>
<tr>
<td>3-Methylfuran + NO₃</td>
<td>2-Methyl-2-butene</td>
<td>1.36±0.02</td>
<td>0.13±0.01</td>
<td></td>
<td>Loop/GC-FID</td>
<td>This work</td>
</tr>
<tr>
<td>2-Methyl-2-butene</td>
<td></td>
<td>1.01±0.05</td>
<td>0.09±0.02</td>
<td>0.13±0.02²</td>
<td>FTIR</td>
<td>This work</td>
</tr>
<tr>
<td>α-Pinene</td>
<td></td>
<td>2.0±0.1</td>
<td>0.116±0.009</td>
<td></td>
<td>FTIR</td>
<td>This work</td>
</tr>
<tr>
<td>2-Methyl-2-butene</td>
<td></td>
<td>-</td>
<td>-</td>
<td>0.13±0.05</td>
<td>GC/FID</td>
<td>Alvarado et al., 1996</td>
</tr>
<tr>
<td>2,3-Dimethyl-2-butene</td>
<td></td>
<td>-</td>
<td>-</td>
<td>0.286±0.006</td>
<td>GC/FID</td>
<td>Kind et al., 1996</td>
</tr>
</tbody>
</table>

²Indicated errors are two least-squares standard deviations. ³Placed on an absolute basis by use of rate constants $k_R$ for the reactions of OH radicals with trans-2-butene, 5-methylfurfural and propene at 298 K of $(7.31±1.31)\times10^{-11}$ cm⁻³molec⁻¹s⁻¹ (Edney et al., 1986), $(5.10±0.20)\times10^{-11}$ cm⁻³molec⁻¹s⁻¹ (Bierbach et al., 1995) and $(3.01±0.42)\times10^{-12}$ cm⁻³molec⁻¹s⁻¹ (Nielsen et al., 1990), respectively; and a rate constant $k_R$ for the reactions of NO₃ radicals with 2-methyl-2-butene and α-Pinene of $(9.38±3.32)\times10^{-12}$ cm⁻³molec⁻¹s⁻¹ (Atkinson, 1991) and $(5.90±0.4)\times10^{-12}$ (Martínez et al., 1998). ⁴Weighted mean.
Table 2: Yields of the products (%C) detected in the reaction of 3-methylfuran with chlorine atoms at room temperature and atmospheric pressure. The errors quoted in the table are a combination of the 2σ 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.

<table>
<thead>
<tr>
<th>Reaction products</th>
<th>Molar Yield (%)</th>
<th>SPME/GC-FID</th>
<th>FTIR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rt (min)</strong></td>
<td><strong>MW</strong></td>
<td><strong>name</strong></td>
<td><strong>Structure</strong></td>
</tr>
<tr>
<td>9.7</td>
<td>96</td>
<td>3-furaldehyde</td>
<td></td>
</tr>
<tr>
<td>9.8</td>
<td>98</td>
<td>Isomer of 3-methyl-2(5H)-furanone</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>16.7</td>
<td>112</td>
<td>3-methyl-2,5-furanodione</td>
<td></td>
</tr>
<tr>
<td>11.4/11.8</td>
<td>98</td>
<td>2-methylbutenedial</td>
<td>HOC-CH=C(CH&lt;sub&gt;3&lt;/sub&gt;)-CHO</td>
</tr>
<tr>
<td>18</td>
<td>98</td>
<td>3-methyl-2(3H)-furanone</td>
<td></td>
</tr>
<tr>
<td>20.9</td>
<td>132</td>
<td>5-chloro-3-methyl-2(5H)-furanone</td>
<td></td>
</tr>
<tr>
<td>23.9</td>
<td>132</td>
<td>5-chloro-4-methyl-2(5H)-furanone</td>
<td></td>
</tr>
<tr>
<td>28.2</td>
<td>114</td>
<td>5-hydroxy-3-methyl-2(5H)-furanone</td>
<td></td>
</tr>
<tr>
<td>Reaction products</td>
<td>Molar Yield (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------------------</td>
<td>-----------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rt (min)</td>
<td>MW</td>
<td>name</td>
<td>Structure</td>
</tr>
<tr>
<td>30.2</td>
<td>114</td>
<td>5-hydroxy-4-methyl-2(5H)-furanone</td>
<td>detected</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrochloric acid</td>
<td>HCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Carbon monoxide</td>
<td>CO</td>
</tr>
</tbody>
</table>

<sup>a</sup> Average of 5 experiments with UV lamps  
<sup>b</sup> only 1 experiment with VIS lamps  
<sup>c</sup> Average of 8 experiments with UV and VIS lamps
Table 3. Atmospheric lifetimes for 3-methylfuran.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>k / 10^{-10} cm^3 molecule^{-1} s^{-1}</th>
<th>τ / h</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>0.91</td>
<td>2.46^a</td>
</tr>
<tr>
<td>NO_3</td>
<td>0.131</td>
<td>1.10^b</td>
</tr>
<tr>
<td>Cl</td>
<td>4.2</td>
<td>66.14^c,d</td>
</tr>
<tr>
<td>O_3</td>
<td>2.05x10^{-7}</td>
<td>18.22^e,f</td>
</tr>
</tbody>
</table>

^a,b Estimated on the basis of the average concentrations in the troposphere of [OH]= 1x10^6 radicals cm^{-3} (Prinn et al., 1992) and [NO_3]= 2x10^7 radicals cm^{-3} (Finlayson Pitts and Pitts, 2000) respectively. ^c,d Estimated on the basis of kinetic rate coefficient for the reaction with Cl atoms at 298 K (Cabañas et al., 2005) and on the basis of the average concentrations in the troposphere of [Cl]= 1x10^4 atoms cm^{-3} (Wingenter et al., 1996). ^e,f Estimated on the basis of kinetic rate coefficient for the reaction with O_3 molecules at 298 K (Alvarado et al., 1996) and on the basis of the average concentrations in the troposphere of [O_3]= 7.4x10^{11} molecule cm^{-3} (Logan, 1985).
Figure 1. Experimental chromatograms and the reaction products identified for the reactions of 3-methylfuran with chlorine atoms (A), hydroxyl radicals (B) and nitrate radicals (C) from SPME-GC/MS experiments.
Figure 2. Concentration-time profiles of 3-methylfuran and products identified in the reaction of 3-
methylfuran with Cl atoms analyzed by SPME-GC-FID: (■) 3-methylfuran, (♦) 3-furaldehyde, (♦) furanone isomer, C₅H₆O₂, (▲) 2-methylbutenedial, (♦) 3-methyl-2(3H)-furanone, (♦) 3-methyl-2,5-
furanodione, (▲) chlorinated methylfuranone (20.9 min), (●) chlorinated methylfuranone (23.9 min).
Figure 3. Experimental infrared absorption spectra from the reaction of: (A) 3-methylfuran with chlorine atoms (a) before photolysis, (b) after 15 min of photolysis (c) residual spectrum from b after subtraction of 3-methylfuran, H₂O with the CO₂ absorption zeroed; (B) 3-methylfuran with hydroxyl radical (residual spectrum of products after 8 min of reaction), (C) 3-methylfuran with nitrate radicals (residual spectrum of products after 3.4 min of reaction).
Scheme 1. Possible mechanisms for the formation of 2-methylbutenedial in the reaction of 3-methylfuran with Cl, OH and NO₃.
Scheme 2. Possible mechanism for the formation of 3-methyl-2(5H)-furanone from 2-methylbutenedial.
Scheme 3. Possible mechanisms for the formation of 3-methyl-2,5-furanodione in the reaction of 2-methylbutenodial with X, where X: Cl, OH or NO₃.
Scheme 4. Possible mechanisms for the formation of 3-furaldehyde in the reaction of 3-methylfuran with X, where X: Cl, OH or NO₃.
Scheme 5. Reaction sequences of 3-methylfuran and X radical initiated by an addition process: possible mechanism for the formation of 5-X-3-methyl-2(5H)-furanone and 5-X-4-methyl-2(5H)-furanone and epoxy furan compounds. X: Cl, OH or NO₃. Compounds C/C’ F/F’ have been not detected.

(1) 5-X-3-methylfuran peroxy radical
(2) 5-X-4-methylfuran peroxy radical
(3) 5-X-3-methylfuran alkoxy radical
(4) 5-X-4-methylfuran alkoxy radical
Scheme 6. Possible mechanisms for the formation of 3-methyl-2,5-furanodione, 5-hydroxy-3-methyl-2(5H)-furanone and 5-hydroxy-4-methyl-2(5H)-furanone from the reaction of 3-methylfuran with X, where X: Cl or NO₃.