

1 **Atmospheric degradation of 3-methylfuran: kinetic and**  
2 **products study**

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1 **Abstract**

2 A study of the kinetics and products obtained from the reactions of 3-methylfuran with  
3 the main atmospheric oxidants has been performed. The rate coefficients for the gas-  
4 phase reaction of 3-methylfuran with OH and NO<sub>3</sub> radicals have been determined at  
5 room temperature and atmospheric pressure (air and N<sub>2</sub> as bath gases), using a relative  
6 method with different experimental techniques. The rate coefficients obtained for these  
7 reactions were (in units cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>): k<sub>OH</sub> = (1.13 ± 0.22) × 10<sup>-10</sup> and k<sub>NO<sub>3</sub></sub> = (1.26  
8 ± 0.18) × 10<sup>-11</sup>. The products from the reaction of 3-methylfuran with OH, NO<sub>3</sub> and Cl  
9 atoms in the absence and in the presence of NO have also been determined. The main  
10 reaction products obtained were chlorinated methylfuranones and hydroxy-  
11 methylfuranones for the reaction of 3-methylfuran with Cl atoms, 2-methylbutenedial,  
12 3-methyl-2,5-furanodione and hydroxy-methylfuranones for the reaction of 3-  
13 methylfuran with OH and NO<sub>3</sub> radicals and also nitrated compounds for the reaction  
14 with NO<sub>3</sub> radicals. The results indicate that in all cases the main reaction path is  
15 addition to the double bond of the aromatic ring followed by ring opening in the case of  
16 OH and NO<sub>3</sub> radicals. The formation of 3-furaldehyde and hydroxy-methylfuranones (in  
17 the reactions of 3-methylfuran with Cl atoms and NO<sub>3</sub> radicals) confirmed the H-atom  
18 abstraction from the methyl group and from the aromatic ring, respectively. This study  
19 represents the first product determination for Cl atoms and the NO<sub>3</sub> radical in reactions  
20 with 3-methylfuran. The reaction mechanisms and atmospheric implications of the  
21 reactions under consideration are also discussed.

## 1 **1. Introduction**

2 3-Methylfuran is a furan derivative that is released into the atmosphere during the  
3 combustion of fossil fuels, waste, biomass and from the isoprene degradation (Graedel  
4 et al., 1986; Soyer et al., 1988; Atkinson et al., 1989; Bierbach et al., 1994; Andreae and  
5 Merlet, 2001). In ambient air, 3-methylfuran has been measured above a rural forested  
6 site with mean daytime mixing ratios estimated at 60 ppt and night-time levels of 40 ppt  
7 (Montzka et al., 1995).

8 Mixing ratios of 3-methylfuran were highly correlated with isoprene (Atkinson et al.,  
9 1984; Gu et al., 1995; Lee et al., 2005). Isoprene is the most abundant biogenic  
10 hydrocarbon emitted into the atmosphere with a global emission rate between 250 and  
11 500 Tg/yr, exceeding that of anthropogenic hydrocarbons (Muller, 1992; Guenther et  
12 al., 1995 and 2006; Laothawornkitkul et al., 2009). The reaction of isoprene with OH  
13 forms 3-methylfuran in an approximate yield of 3–7% depending presumably on the  
14 pressure (Ruppert and Becker, 2000; Lee et al., 2005). Therefore, and due to the high  
15 emission rates of isoprene, the potential atmospheric significance of the oxidation  
16 products (3-methylfuran) consequently increases.

17 3-Methylfuran is expected to be very reactive with the main atmospheric oxidants.  
18 According to Atkinson et al. (1989), 3-methylfuran may play a role, albeit minor, in the  
19 chemical cycles in the lower troposphere. To date very few kinetic studies have been  
20 published concerning 3-methylfuran. Indeed, only one value has been reported for the  
21 rate coefficient at room temperature for the reaction of the OH radical with 3-  
22 methylfuran using a relative technique (Atkinson et al., 1989). Furthermore, two kinetic  
23 studies on the reaction of 3-methylfuran with the NO<sub>3</sub> radical have been published  
24 (Kind et al., 1996; Alvarado et al., 1996) and these gave two very different values for  
25 the rate coefficient. In the case of the reaction with Cl atoms, the rate coefficient  
26 reported in the literature was obtained by our research group in a previous work  
27 (Cabañas et al., 2005).

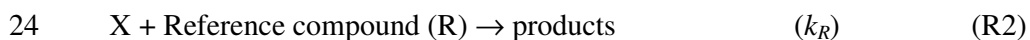
28 With respect to reaction products, the data available in the literature are especially  
29 scarce. Only a recent product study for the photooxidation with HONO of 3-  
30 methylfuran indicates that 2-methylbutenedial is the main gaseous product of the OH-  
31 oxidation of this compound (Gómez Álvarez et al., 2009). A theoretical computational  
32 study has also been published for this reaction and the conclusion was that direct

1 hydrogen abstraction and nucleophilic bimolecular substitution play a minor or  
2 negligible role in the overall reaction (Zhang et al., 2008).  
3 Therefore, in the work described here rate coefficients for the reaction of OH and NO<sub>3</sub>  
4 radicals with 3-methylfuran were determined in order to (i) assess the values previously  
5 reported in the literature as they show discrepancies and (ii) to complete the kinetic  
6 study of alkylfurans initiated by our research group. Experiments were carried out at  
7 (298 ± 2) K and a total pressure of 1 atm using a relative rate method with  
8 LOOP/SPME-GC/FID/MS (Loop/Solid Phase Microextraction-Gas Chromatography/  
9 Flame Ionization Detection/Mass Spectrometry Detection) and FTIR (Fourier  
10 Transform Infrared Spectroscopy) as detection techniques for the organic compounds.  
11 Products obtained in the reaction of 3-methylfuran with OH and NO<sub>3</sub> radicals and with  
12 Cl atoms were also characterized in order to propose degradation mechanisms for this  
13 compound in the atmosphere. This reaction product study was carried out using SPME-  
14 GC/FID/MS and FTIR as detection methods.

## 15 **2. Experimental section**

### 16 **2.1. Kinetic study**

17 Rate coefficient for the gas phase reactions of 3-methylfuran with the atmospheric  
18 oxidants, OH and NO<sub>3</sub> radicals, at (298 ± 2) K and ~1 atm of total pressure in synthetic  
19 air and N<sub>2</sub>, respectively, was determined using a relative rate method. In the  
20 experiments the reactions of 3-methylfuran and reference compounds (with rate  
21 coefficients  $k_S$  and  $k_R$ , respectively) were monitored in the presence of OH or NO<sub>3</sub>  
22 radicals:



25 where X is OH or NO<sub>3</sub>

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

$$29 \quad \ln\left(\frac{[S]_0}{[S]_t}\right) = \frac{k_S}{k_R} \ln\left(\frac{[R]_0}{[R]_t}\right) \quad (1)$$

30 Thus, a plot of  $\ln([S]_0/[S]_t)$  versus  $\ln([R]_0/[R]_t)$  should be a straight line passing through  
31 the origin and whose slope gives the ratio of rate coefficients  $k_S/k_R$ . Each reaction

1 studied was measured relative to the reaction of different reference standards with  
2 oxidants X. In the case of 3-methylfuran with NO<sub>3</sub>, a dilution term was included in Eq.  
3 (1) due to the special experimental procedure, which is described below. Therefore, for  
4 this reaction the equation required to obtain the rate coefficient is:

$$5 \quad \ln\left(\frac{[S]_0}{[S]_t}\right) - D_t = \frac{k_s}{k_R} \left( \ln\left(\frac{[R]_0}{[R]_t}\right) - D_t \right) \quad (2)$$

6 Where D<sub>t</sub> is calculated as D<sub>t</sub> = ln([I]<sub>0</sub>/[I]<sub>t</sub>) and I is an internal standard.

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

13 The experimental systems and the procedures used in this work are briefly described  
14 below. Further details can be found elsewhere (Cabañas et al., 2008; Villanueva et al.,  
15 2007; 2009). Only the FTIR system with a 50 L Pyrex glass vessel is described below in  
16 detail.

17 Experiments were performed using three analytical systems: gas chromatography with  
18 flame ionization detection (GC/FID), gas chromatography with mass spectrometry  
19 detection (GC/MS) and Fourier transform infrared absorption spectroscopy (FTIR). In  
20 the kinetic experiments carried out with gas chromatography, two evacuable Teflon-  
21 coated bags (Adtech) were used – one with a volume of 150 L for the experiments with  
22 OH radicals and one of 500 L for the experiments with NO<sub>3</sub> in order to minimize the  
23 dilution effect of the additions of N<sub>2</sub>O<sub>5</sub>. These bags were placed inside a rectangular  
24 cage with six VIS lamps (λ<sub>max</sub> = 360 nm) mounted on the walls. A system based on  
25 sample preconcentration, the solid phase microextraction technique (SPME) and a  
26 heated loop of 1 cm<sup>3</sup> capacity mounted in a six way valve were used as sampling  
27 methods. In the first case the samples were collected for 15 min by exposing a 50/30  
28 mm DVB/CAR/PDMS fibre to the reaction mixture in the Teflon bag. The fibre was  
29 then thermally desorbed for 10 min at 270 °C in the heated GC injection port. In the  
30 second case the reaction mixture was slowly pumped through the sampling loop to  
31 ensure that it was thoroughly flushed and then allowed to come to equilibrium with a  
32 reaction chamber pressure of 1 atm prior to injection. The concentrations of 3-

1 methylfuran and the reference compounds were followed by means of capillary gas  
2 chromatography and detection by FID or MS. In all experiments a capillary column  
3 (30m × 0.32mm id × 1.0 μm film thickness, Tracsil TRB-1701, Teknokroma) was used  
4 to separate the compounds. The chromatographic conditions used for the analysis were  
5 as follows: injector, 270 °C; detector, 250 °C, the temperature program was from 40 °C  
6 (4 min) to 120°C (17 min) at a rate of 25 °C min<sup>-1</sup>.

7 The in situ FTIR analysis of 3-methylfuran with OH and NO<sub>3</sub> radicals was carried out in  
8 a 50 L Pyrex glass reaction chamber at a total pressure of approximately 1 atm and (298  
9 ± 2) K in synthetic air. The reactants were injected into the reaction chamber using a  
10 vacuum line. A pumping system consisting of a rotary pump (Varian DS 302) was used  
11 to evacuate the reactor after every experiment. The photolysis system consisted of eight  
12 actinic fluorescent lamps (λ<sub>max</sub> = 360 nm) spaced evenly around the reaction chamber.  
13 The chamber was equipped with a White-type multiple-reflection mirror system (Saturn  
14 Series Multi-Pass cells) with a base length of 1.35 m for sensitive in situ long path  
15 absorption monitoring of reactants and products in the IR spectral range 4000–650 cm<sup>-1</sup>.  
16 The White system can operate at 72 traverses, giving a total optical path length of 200  
17 m. The IR spectra were recorded with a resolution of 1 cm<sup>-1</sup> using a Thermo Nicolet  
18 5700 FT-IR spectrophotometer equipped with a KBr beam splitter and a liquid nitrogen  
19 cooled mercury–cadmium–telluride (MCT) detector. Typically, for each spectrum, 60  
20 interferograms were co-added over 2 min and approximately 30 such spectra were  
21 recorded per experiment. Hydroxyl radicals were generated in the presence of NO by  
22 the photolysis of CH<sub>3</sub>ONO in air (Atkinson et al., 1981) at wavelengths of 360 nm using  
23 the VIS lamps.

24 The techniques and the reference compounds used in the reactions of 3-methylfuran  
25 with OH and NO<sub>3</sub> radicals are listed in Table 1.

26 In the experiments performed with LOOP/GC-MS, benzene was used as the internal  
27 standard. The reactant mixtures were photolyzed for 0.5–2.0 min and a gas  
28 chromatogram or an IR spectrum of the chamber contents was recorded. This  
29 photolysis-sampling procedure was repeated until around 54–93% depletion of the 3-  
30 methylfuran and 41–83% depletion of the reference compound were achieved.  
31 Typically six to seventeen photolysis-sampling steps were carried out during each  
32 experiment.

1 Nitrate radicals were generated in situ in the dark by the thermal decomposition of  $\text{N}_2\text{O}_5$   
2 (Atkinson et al., 1984; Atkinson et al., 1988). During GC-FID experiments successive  
3 additions of  $\text{N}_2\text{O}_5$  ( $2.5 \times 10^{13}$ – $1.1 \times 10^{14}$  molecule  $\text{cm}^{-3}$ ) were performed. Sampling was  
4 carried out approximately 7 min after the addition of  $\text{N}_2\text{O}_5$  and at subsequent intervals  
5 of 18 min. A total of nine additions were typically made in each experiment. This  
6 procedure allowed a depletion for 3-methylfuran of 81% and a depletion for the  
7 reference compound of 72% to be achieved. In FTIR experiments only one addition of  
8  $\text{N}_2\text{O}_5$  at ( $1.1 \times 10^{15}$ ) molecule  $\text{cm}^{-3}$  was performed. This procedure allowed a depletion  
9 for 3-methylfuran of 58–100% and a depletion for the reference compound of 59–96%  
10 to be achieved.

11 The initial reactant concentrations in the reactors (in molecule  $\text{cm}^{-3}$ ) were as follows:  
12 [3-methylfuran] =  $(2\text{--}9) \times 10^{14}$ , [reference] =  $(1.5\text{--}9) \times 10^{14}$  [ $\text{CH}_3\text{ONO}$ ] =  $(3\text{--}15) \times 10^{14}$   
13 [ $\text{NO}$ ] =  $(2\text{--}28) \times 10^{14}$  and [benzene] =  $(4\text{--}15) \times 10^{14}$ .

## 14 **2.2. Products study**

15 Product experiments were carried out at  $(298 \pm 2)$  K and at atmospheric pressure of air  
16 in different reaction chambers: (a) in a 150 L evacuable Teflon-coated chamber  
17 equipped with six 360 nm lamps and four 254 nm lamps and with provision for  
18 sampling onto a 30/50  $\mu\text{m}$  SPME (DVB/CAR/PDMS) fibre. The fibre adsorption and  
19 desorption time was 15 min at 270 °C in split/splitless mode for the GC injection port.  
20 The analysis in this case was carried out using GC/MS and GC/FID. Products were  
21 separated in the capillary column by applying the following temperature program: from  
22 40 °C (4 min) to 120 °C (12 min) at a rate of 25 °C  $\text{min}^{-1}$ , then at a rate of 10 °C  $\text{min}^{-1}$   
23 up to 200 °C (10 min). Mass spectrometry detection was performed in electron impact  
24 mode with a detector temperature of 230 °C. These experimental systems were used for  
25 the reactions of 3-methylfuran with OH and  $\text{NO}_3$  radicals and Cl atoms; (b) in a 50 L  
26 Pyrex glass cell equipped with eight actinic fluorescent lamps ( $\lambda_{\text{max}} = 360$  nm) with in  
27 situ FTIR analysis for OH and  $\text{NO}_3$  radicals; and (c) in a 1080 L quartz-glass reactor  
28 equipped with 10 low-pressure mercury lamps ( $\lambda_{\text{max}} = 254$  nm) and 10 superactinic  
29 fluorescence lamps ( $\lambda_{\text{max}} = 360$  nm) coupled with in situ FTIR analysis for Cl atoms.  
30 Details of this experimental set-up can be found elsewhere (Barnes et al. 1994).  
31 In the quantitative analysis carried out by GC/FID, the response factor (RF) of each  
32 compound was determined by introducing different measured amounts of authentic

1 standards (which covered the range of experimental conditions) into the Teflon chamber  
2 and conducting several replicate analyses with the coated SPME fibre. For compounds  
3 that were not commercially available or the synthesis yield of the pure compound was  
4 not sufficient to carry out the calibration, only an estimation of yield was possible using  
5 the ECN (effective carbon number) method (Scalon and Willis, 1985).

6 The response factor of each compound was calculated with the expression:

$$7 \quad \text{Area} = \text{RF} \times [\text{product}] \quad (3)$$

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

11 In the FTIR analysis a spectral subtraction procedure was used to derive the  
12 concentrations of 3-methylfuran and products as a function of the reaction time.  
13 Identification and quantification of 3-methylfuran and products in the case of Cl  
14 reactions was carried out using calibrated reference spectra. The calibrated spectra were  
15 either produced by introducing a known concentration of an authentic sample of the  
16 compound into the reactor or were taken from an existing IR spectral library bank.

17 Yields were calculated by plotting the amounts of product formed at each time  $t$  against  
18 the amounts of 3-methylfuran consumed at each time  $t$ .

### 19 **2.2.1. Cl products**

20 Different techniques were used to identify and quantify the reaction products at  $(298 \pm$   
21  $2)$  K and atmospheric pressure. The experiments involving SPME GC/MS and  
22 GC/FID/ECD techniques were conducted in  $\approx 150$  L Teflon bag placed inside a chamber  
23 with four 254 nm blacklamps. Photolysis of thionyl chloride ( $\text{SOCl}_2$ ) or trichloroacetyl  
24 chloride ( $\text{CCl}_3\text{COCl}$ ) was used to generate atomic chlorine in irradiation steps of 8 to 10  
25 seconds for  $\text{SOCl}_2$  and 10 to 60 s for  $\text{CCl}_3\text{COCl}$ . The total photolysis time was 30–90 s  
26 for  $\text{SOCl}_2$  and 22–720 s for  $\text{CCl}_3\text{COCl}$  with a conversion of 3-methylfuran between 21  
27 and 94%.  $\text{Cl}_2$  was not used as the source of Cl atoms because  $\text{Cl}_2$  reacts with 3-  
28 methylfuran at the concentration used for this study. All experiments were carried out in  
29 the absence of NO and only one qualitative experiment was carried out in the presence  
30 of NO. The initial concentrations of the reactants in the qualitative analysis (in molecule  
31  $\text{cm}^{-3}$  units) were:  $[\text{3-methylfuran}] = (4.9\text{--}29) \times 10^{13}$ ,  $[\text{CCl}_3\text{COCl}] = (1.4\text{--}2.4) \times 10^{14}$ ,



1 [SOCl<sub>2</sub>] = (4.4–19) × 10<sup>13</sup> and [NO] = 3.4 × 10<sup>13</sup>. Electron impact (EI) and chemical  
2 ionization (CI with methane as the ionization gas) modes were used in mass  
3 spectrometry detection in order to identify and obtain molecular weight information on  
4 the different reaction products. In addition, an electron capture detector (ECD) was used  
5 to identify some reaction products. The quantitative analysis was performed in the  
6 GC/FID using SOCl<sub>2</sub> as the CI source. The concentrations used were (7.3–14) × 10<sup>13</sup>  
7 and (7.3–15) × 10<sup>13</sup> molecule cm<sup>-3</sup> for 3-methylfuran and SOCl<sub>2</sub>, respectively. The total  
8 photolysis time was 60–100 s in order to achieve a conversion of 3-methylfuran of 60–  
9 90%.

10 In FTIR experiments a cylindrical quartz-glass reactor of 1080 L was used. Cl atoms  
11 were generated by the photolysis of ClCOCOCl and Cl<sub>2</sub> using 10 low-pressure mercury  
12 lamps and 8 superactinic fluorescence lamps, respectively. The total photolysis time  
13 was 11–25 min for ClCOCOCl and 23 min for Cl<sub>2</sub> and under these conditions the 3-  
14 methylfuran conversion was 33–95%. The reactions between 3-methylfuran and Cl<sub>2</sub>  
15 were found to be negligible in the quartz-glass reactor under the conditions used. The  
16 use of molecular chlorine as the source of Cl atoms therefore avoided potential  
17 photolysis at 254 nm of the products generated in the reaction.

18 The initial concentrations of the reactants (in molecule cm<sup>-3</sup> units) were: [3-  
19 methylfuran] = (1.9–2.9) × 10<sup>13</sup>, [Cl<sub>2</sub>] = (4.9–7.3) × 10<sup>13</sup> and [ClCOCOCl] = 1.2 × 10<sup>13</sup>.  
20 The reactants were injected directly into the reaction chamber using calibrated gas-tight  
21 syringes through an inlet port located on one of the chamber end flanges and the  
22 chamber was pressurised to 1 atm total pressure with air. The reactant and the products  
23 were monitored in situ using a multi-reflection White mirror system (5.6 m base length,  
24 498 m total path length) mounted in the reactor and coupled to an FTIR  
25 spectrophotometer (Thermo Nicolet Nexus) equipped with a KBr beam splitter and  
26 MCT detector. The IR spectra were recorded in the 700–4000 cm<sup>-1</sup> spectral range with  
27 1 cm<sup>-1</sup> resolution by co-adding 64 interferograms over 60 s. In typical experiments 25  
28 spectra were recorded over a period of 25 min with light.

### 29 **2.2.2. OH products**

30 The qualitative determination of products was carried out using GC/MS and  
31 FTIR analysis and quantitative determination was performed using GC/FID (Acme 6100  
32 GC Young). Two OH precursors were used in the products studies by GC/MS in order to



1 +99%), propene (Aldrich, +99%), 2-methyl-2-butene (Aldrich, +99%), Cl<sub>2</sub> (Praxair,  
2 >99.8%), N<sub>2</sub> (Praxair, 99.999%), air (Praxair, 99.999%) and NO (Praxair, 99%). The  
3 following compounds were used in methylnitrite synthesis: NaNO<sub>2</sub> (Panreac, 97%),  
4 H<sub>2</sub>SO<sub>4</sub> (Panreac, 95–98%) and CaCO<sub>3</sub> (Riedel-de-Haën AG, 99%). In N<sub>2</sub>O<sub>5</sub> synthesis:  
5 N<sub>2</sub>O<sub>4</sub> (Fluka, >98.5%) and O<sub>2</sub> (Praxair, 99.999%). Hydroxymethyl-2(5*H*)-furanones [5-  
6 hydroxy-3-methyl-(5*H*)-furanone and 5-hydroxy-4-methyl-2(5*H*)-furanone] were  
7 prepared from 3-methylfuran according to Kumar and Pandey (2000). The product was  
8 characterised by GC-MS.

### 9 **3. Results and discussion**

#### 10 **3.1. Kinetic studies**

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

19 The weighted mean  $k_S$  values and the rate coefficient ratios  $k_S/k_R$  obtained from least-  
20 squares analyses using GC/FID and FTIR techniques are given in Table 1. The data  
21 show that within error there is no significant difference between runs by GC/FID/MS or  
22 FTIR. As can be seen from the results in Table 1, the high values of the OH rate  
23 coefficients (in the order of  $10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) show the high reactivity of OH  
24 radicals towards 3-methylfuran. Available literature data are also shown in Table 1. It  
25 can be observed that the weighted mean rate coefficient data for the reaction of 3-  
26 methylfuran with OH are slightly higher than the literature data (Atkinson et al., 1989)  
27 but these can be considered similar due to experimental errors. The rate coefficients for  
28 OH reactions can be estimated by the AOPWIM program from the SAR method  
29 (Aschmann and Atkinson, 1995). The value of rate constant for 3-methylfuran and OH  
30 calculated in this way is  $1.05 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which is similar to the average  
31 rate coefficient value obtained in this work.

1 In relation to reaction of 3-methylfuran with  $\text{NO}_3$ , the rate constant obtained in this  
2 work is consistent with the data obtained by Alvarado et al. (1996). Therefore a mean  
3 value between the rate constants for OH and  $\text{NO}_3$  radicals determined in this study and  
4 the ones obtained by Atkinson et al. (1989) and Alvarado et al. (1996) respectively can  
5 be proposed as good reference data.

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

## 12 **3.2. Products studies**

13 The major challenge in identifying the reaction products from the reaction of 3-  
14 methylfuran with OH,  $\text{NO}_3$  radicals and Cl atoms is the scarcity of commercially  
15 available standards. The identification of reaction products was carried out using the  
16 custom GC-MS and FTIR libraries created after the injection of commercial products  
17 [3-furaldehyde, 3-methyl-2,5-furanodione, 3-methyl-2(5*H*)-furanone, 5-hydroxy-4-  
18 methyl-2(5*H*)-furanone, crotonaldehyde, acetic acid, 2-methyl-propenoic acid and 2-  
19 butenoic acid], or compounds synthesized in our laboratory [2-methylbutenedial, 5-  
20 hydroxy-3-methyl-(5*H*)-furanone and 5-hydroxy-4-methyl-2(5*H*)-furanone] or using  
21 commercial GC-MS library (NIST 21, NIST 27, NIST 107, NIST 147 and WILEY 229)  
22 and Aldrich Library FTIR spectra (Pouchert, C.J., 1989). The results are explained in  
23 detail below for each reaction.

### 24 **3.2.1. Reaction with Cl atoms**

25 An example of a typical chromatogram is shown in Figure 1A for the oxidation of 3-  
26 methylfuran by Cl atoms in the absence of NO at different reaction times and in the  
27 presence of NO (upper chromatogram). Peaks A and C represent artefact compounds  
28 from the chlorine source and from the fibre, respectively. 3-Methylfuran is represented  
29 by peak B. The only compounds identified by the mass spectra and by the retention  
30 times of authentic standards are 3-furaldehyde (peak D), 3-methyl-2,5-furanodione  
31 (peak H) and 3-methyl-2(3*H*)-furanone (peak I). Analysis of the EI mass spectrum of  
32 peak E shows the presence of the compound  $\text{C}_5\text{H}_6\text{O}_2$  and the chemical ionization (CI)

1 mass spectrum of this peak shows that its molecular weight is 98. This peak can  
2 therefore be tentatively assigned to an isomer of 3-methyl-2(3*H*)-furanone or 2-  
3 methylbutenedial. Peaks F and G are assigned to (*E/Z*)-2-methylbutenedial based on the  
4 EI fragmentation and by comparison of the mass spectrum with the reference mass  
5 spectrum and the retention time of the synthesized compound. Peaks L and M are  
6 assigned to 5-hydroxy-3-methyl-2(5*H*)-furanone and 5-hydroxy-4-methyl-2(5*H*)-  
7 furanone, respectively, based on EI fragmentations and the CI mass spectra, which  
8 indicate that the molecular weight is 114 (see Figure 3 in supporting information). The  
9 synthesis of the isomers of hydroxy-methylfuranones confirmed the presence of these  
10 compounds by comparison with the mass spectra and retention times. Furthermore,  
11 comparison with the commercial 5-hydroxy-4-methyl-2(5*H*)-furanone confirmed that  
12 this compound gave rise to peak M. Peaks J and K – with retention times of 20.9 and  
13 23.9 min, respectively – are the most intense and were identified as chlorinated organic  
14 compounds of molecular formula C<sub>5</sub>H<sub>5</sub>O<sub>2</sub>Cl based on the following evidence: (a) the CI  
15 mass spectrum shows that the molecular ion is at *m/z* 132, (b) the fragmentation pattern  
16 from the electron impact mass spectrum is also consistent with this compound and (c)  
17 the gas chromatogram obtained with electron capture detection (ECD), which is  
18 particularly sensitive to chlorinated compounds, shows only two intense peaks at 20.9  
19 and 23.9 min. Additionally, in previous experiments 5-chloro-2(5*H*)-furanone was  
20 detected as a product from the reactions of furan (Villanueva et al., 2007), 2-  
21 methylfuran and 2-ethylfuran (Villanueva et al., 2009) with Cl atoms, therefore it is  
22 believed that peaks J and K could be assigned to chlorinated methylfuranones [5-chloro-  
23 3-methyl-2(5*H*)-furanone and 5-chloro-4-methyl-2(5*H*)-furanone]. Peaks J and K could  
24 also be assigned to acid chlorides (3-methyl-4-oxo-2-butenoyl chloride or 2-methyl-4-  
25 oxo-2-butenoyl chloride) [HOC–CH=C(CH<sub>3</sub>)–COOH] in the same way as 4-oxo-2-  
26 pentenoyl chloride was identified in the reaction of 2-methylfuran with Cl atoms. Both  
27 chlorinated methylfuranones and acid chlorides could be formed by the addition of Cl to  
28 the two ortho positions. The EI and CI mass spectra of peaks J and K are shown in  
29 Figure 4 (in supporting information). The molecular ion peak in the CI mass spectrum  
30 (MW 132) shows a fragment from a more stable ion [*M* + 1 – 34 = 99 da]. As described  
31 below for the FTIR analysis, the chlorinated methylfuranones are probably the  
32 compounds that are formed to the greatest extent. As shown in Figure 1A the reaction

1 products in the absence and in the presence of NO are similar. The only difference  
2 probably concerns the yields.

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

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

20 FTIR spectra recorded for different stages of the reaction of 3-methylfuran with Cl are  
21 shown in Figure 3A: (a) spectrum of 3-methylfuran+Cl<sub>2</sub> in air before photolysis, (b)  
22 spectrum of 3-methylfuran and products after 15 min of photolysis (absorptions from  
23 CO<sub>2</sub> have been zeroed due to saturation of the band and those from H<sub>2</sub>O have been  
24 subtracted), and (c) the residual product spectrum after subtraction of 3-methylfuran.

25 The residual spectrum of the products shows the presence of HCl and CO, a band with a  
26 high intensity at 1825 cm<sup>-1</sup>, bands of medium intensity in the region 800–1300 cm<sup>-1</sup> and  
27 two bands of low intensity in the carbonyl region at 1710 and 1665 cm<sup>-1</sup>. Based on the  
28 results obtained by SPME-GC/MS the band at 1710 cm<sup>-1</sup> is assigned to 3-furaldehyde –  
29 an assignment also based on a comparison with the reference spectrum. The bands at  
30 1703 and 1665 cm<sup>-1</sup> can be tentatively assigned to 2-methylbutenedial, but due to the  
31 low purity of the 2-methylbutenedial synthesized this can not be confirmed from the IR  
32 spectrum. Based on the GC/MS results and those obtained in our previous studies on the  
33 reaction of Cl atoms with furan (Villanueva et al., 2007), 2-methylfuran and 2-

1 ethylfuran (Villanueva et al., 2009), the band at  $1825\text{ cm}^{-1}$  can be assigned to the  
2 chlorinated methylfuranone isomers 5-chloro-3-methyl-2(5*H*)-furanone and 5-chloro-4-  
3 methyl-2(5*H*)-furanone. The band at  $1825\text{ cm}^{-1}$  is very similar in appearance to that  
4 observed in our previous studies for the reaction of Cl atoms with alkylfurans, where the  
5 band at  $1829\text{ cm}^{-1}$  was assigned to 5-chloro-2(5*H*)-furanone and confirmed by  
6 comparison with the reference spectrum of a synthesized sample. The possibility that  
7 the compound was an acid chloride (3-methyl-4-oxo-2-butenoyl chloride or 2-methyl-4-  
8 oxo-2-butenoyl chloride) was ruled out as the infrared spectrum is devoid of any  
9 absorption bands in the region  $2695\text{--}2900\text{ cm}^{-1}$ , which would be characteristic for the  
10 stretching vibration of C–H in the –CHO group.

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

19 The product yields were calculated from the slopes of plots of products formed versus  
20 3-methylfuran reacted; it should be noted that on using UV lamps the secondary  
21 reactions are almost negligible in the early stages of the reaction (Bierbach et al. 1995).  
22 The molar yields obtained for the products identified by SPME/GC-FID and FTIR are  
23 given in Table 2 together with their retention times, molecular weights. The total error  
24 is a combination of statistical error  $2\sigma$  obtained in regression analysis and uncertainties  
25 estimated in the calibrations. Although it was not possible to quantify all of the  
26 identified compounds, if we compare the results from the quantification methods,  
27 SPME-GC/FID and FTIR, it is clear that chlorinated methylfuranones are the major gas-  
28 phase reaction products of the reaction between Cl atoms and 3-methylfuran. Despite  
29 the overall uncertainties associated with each quantification method, the yields of the  
30 products are in fair quantitative agreement. A total carbon mass balance of 70% was  
31 obtained for the products detected in GC-FID experiments and 90% for the products  
32 determined by FTIR. These values must be treated with caution because the yield of  
33 chlorinated methylfuranones could be underestimated by GC-FID, as occurred in the

1 case of the chlorinated furanone formed from furan and alkylfurans with Cl atoms or  
2 overestimated in the case of FTIR (Villanueva et al., 2007, 2009).

### 3 **3.2.2. Reaction with OH radicals**

4 An example of a typical chromatogram of the oxidation of 3-methylfuran by OH  
5 radicals in the presence of NO is shown in Figure 1B. 3-Methylfuran is represented by  
6 peak A. The only compounds identified by the mass spectrum and by the retention time  
7 of authentic standards are acetic acid (peak B), 3-furaldehyde (peak C), 2-  
8 methylbutenedial (peak E), 3-methyl-2,5-furanodione (peak F), 3-methyl-2(3*H*)-  
9 furanone (peak G) and 5-hydroxy-4-methyl-2(5*H*)-furanone (peak I). Peak H is assigned  
10 to 5-hydroxy-3-methyl-2(5*H*)-furanone by comparison with the mass spectrum and  
11 retention time of the synthesized compound. Analysis of the EI mass spectrum of peak  
12 D shows the presence of a compound of formula C<sub>5</sub>H<sub>6</sub>O<sub>2</sub> but this was not assigned to  
13 any particular structure.

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

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

29 In the case of FTIR experiments, and due to low signal intensity, the reaction products  
30 were only tentatively assigned in order to complete or confirm the results from  
31 SPME/GC-MS. The residual FTIR spectrum for the product obtained in the oxidation of  
32 3-methylfuran with OH radicals in the presence of NO is shown in Figure 3B after  
33 subtraction of the spectra of 3-methylfuran, NO<sub>2</sub>, NO, HCHO, HNO<sub>3</sub>, HONO and



1 CH<sub>3</sub>ONO. Only 3-methyl-2,5-furanodione was identified by comparison with the bands  
2 of an authentic standard (898, 1792 and 1858 cm<sup>-1</sup>). Although 2-methylbutenedial was  
3 identified by GC-MS analysis, identification by FTIR was not possible due to the low  
4 purity of the synthesized compound. Thus, the band at 1711 cm<sup>-1</sup> in Figure 3B was  
5 assigned to 2-methylbutenedial by comparison with the bands of other 1,4-dicarbonyl  
6 compounds such as butenedial and based on the results obtained in the GC-MS.

7 2-methylbutenedial, was identified and quantified (yield of (83 ± 33)%) as major  
8 reaction product by Gómez Álvarez et al. (2009) in the study of the degradation of 3-  
9 methylfuran with OH radicals. The low yield (1.4%) obtained in our work could be due  
10 to the occurrence of secondary reactions to form products such as 3-methyl-2(3*H*)-  
11 furanone and 3-methyl-2,5-furanodione. The secondary reactions that imply the loss of  
12 2-methylbutenedial (photolysis process, reaction with OH radical, wall loss, etc) is  
13 supported by several facts: 1)- Bierbach et al. (1995) reported that the yield of 4-oxo-  
14 2-pental (unsaturated 1,4-dicarbonyl) in the reaction of 2-methylfuran with OH  
15 radical varied from ≈70% at the beginning of the reaction to ≈47% at the end. Due to  
16 photolysis of the compound and probably to the oxidation of the dicarbonyl compound  
17 with OH radicals (Bierbach et al., 1994, Tang and Zhu, 2005). 2) -the decay in the  
18 intensity of the band at 1711 cm<sup>-1</sup> with the time in our experiments. From analysis of the  
19 decay of this band (supposing a decay of first order) a rate constant of 0.026 s<sup>-1</sup> can be  
20 estimated what means a very fast loss process. In the next section a possible sequence of  
21 reactions that 2-methylbutenedial can suffer is commented. The reason why secondary  
22 reactions take place in a higher extension in our experiments than in Bierbach et al.  
23 (1995) and Gómez Álvarez et al. (2009) could be due to the different experimental  
24 conditions used.

25 The bands at 795, 1297 and 1734 cm<sup>-1</sup> are typical of nitroperoxy compounds  
26 (ROONO<sub>2</sub>) formed from the reaction of peroxy radicals with NO<sub>2</sub> (Wängberg et al.  
27 1997, Martín et al. 2002). One of the most intense bands is observed at 1820 cm<sup>-1</sup> that  
28 can be assigned to a carbonyl group that together with the band of 1014 cm<sup>-1</sup> typical of  
29 OH group support such as that in the hydroxy-methylfuranones. This assignment is  
30 supported from the displacement that the wavelength of the -CO group suffers to higher  
31 values due to the presence of a -OH group with a positive conjugative effect (+K) in β  
32 position. For example in the 5-ethyl-2-tetrahydrofuranone the band of -CO appears at  
33 1811 cm<sup>-1</sup> while in the 5-hydroxymethyl-2-tetrahydrofuranone this band appears at

1 1823  $\text{cm}^{-1}$  due to the positive conjugative effect of the  $-\text{OH}$  group. On the other hand  
2 the band at 1014  $\text{cm}^{-1}$  can be due to a  $-\text{OH}$  group in  $\beta$  position in relation to a  $-\text{CO}$   
3 group. It is known that groups with a negative conjugative effect ( $-\text{K}$ ) next to a  $-\text{OH}$   
4 groups cause the displacement of the band to lower values. For example,  $\text{C}-\text{OH}$   
5 absorption band of 3-hydroxyfuran appears at 1087  $\text{cm}^{-1}$  and in 4,4-dimethyl-3-  
6 hydroxy-2-furanone appears at 1015  $\text{cm}^{-1}$ . However, hydroxy-methylfuranones was not  
7 confirmed due to the low purity of the commercial compound. In the reaction of 2-  
8 methylfuran with  $\text{OH}$  radicals Bierbach et al. (1995) observed a band at 1820  $\text{cm}^{-1}$  that  
9 was not assigned. Furthermore, Gómez Álvarez et al. (2009), in the reaction of 3-  
10 methylfuran with  $\text{OH}$  radicals (but in the aerosol phase), obtained a compound with a  
11 molecular weight of 114, which was tentatively assigned to 4-keto-pentenoic acid based  
12 on the molecular formula  $\text{C}_5\text{O}_3\text{H}_6$ . This molecular formula also corresponds with 5-  
13 hydroxy-2(5H)-methylfuranone.

14 Based on the intensities of the peaks obtained by GC/MS, and taking into account that  
15 only 24% of the reacted carbon was identified, it is likely that the bands at 1820  $\text{cm}^{-1}$   
16 and 1014  $\text{cm}^{-1}$  are due to the isomers identified by GC/MS. Compounds such as  $\text{CO}$   
17 (2115 and 2176  $\text{cm}^{-1}$ ) and  $\text{CO}_2$  (2360  $\text{cm}^{-1}$ ) are also evident and the intensity of their  
18 bands increase with time, which signifies that open compounds could be forming during  
19 the reaction.

### 20 **3.2.3. Reaction with $\text{NO}_3$ radicals**

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

30 The residual product FTIR spectrum from the oxidation of 3-methylfuran with  $\text{NO}_3$   
31 radicals after subtraction of the spectra of 3-methylfuran,  $\text{N}_2\text{O}_5$ ,  $\text{NO}_2$  and  $\text{HNO}_3$  is  
32 shown in Figure 3C. The bands at 792, 1294 and 1732  $\text{cm}^{-1}$  are assigned to nitroperoxy  
33 compounds ( $-\text{OONO}_2$ ) based on the fact that nitroperoxy compounds decompose with

1 time (Hjorth et al., 1990; Wängberg and Ljungström, 1992) what was confirmed  
2 experimentally.

3 The bands at 857, 1287, 1660 and 1695  $\text{cm}^{-1}$  are assigned to nitrooxy compounds ( $-\text{ONO}_2$ )  
4 considering that the typical bands of this group appear at 843, 1296 and 1672  
5  $\text{cm}^{-1}$  (Tuazon et al., 1999). In our case appear two bands around at 1672  $\text{cm}^{-1}$  (1695 and  
6 1660  $\text{cm}^{-1}$ ). These bands can be explained by the presence of two reaction products. One  
7 product with a hydroxyl group and a  $-\text{ONO}_2$  group, and other product with a carbonyl  
8 group a  $-\text{ONO}_2$  group. So, the presence of an OH group, with positive conjugative  
9 effect (+K), would shift the  $-\text{ONO}_2$  absorption band to a higher wavenumber of 1672  
10  $\text{cm}^{-1}$  such as the band at 1695  $\text{cm}^{-1}$ , likewise a CO group with negative conjugative  
11 effect ( $-K$ ) would shift the  $-\text{ONO}_2$  absorption band to a lower wavenumber of 1672  $\text{cm}^{-1}$   
12 such as the band at 1660  $\text{cm}^{-1}$ . On the other hand the presence of the bands at 1061 and  
13 1090  $\text{cm}^{-1}$  confirm the presence of hydroxynitrate compounds where the nitrate group  
14 displaces the C-OH band to higher wavenumber by the same positive conjugative  
15 effect. In the next section scheme 5 shows the reaction mechanisms for the formation  
16 these compounds. The simultaneous presence of these two sets of bands (792, 1294,  
17 1732 and 857, 1287, 1660, 1695  $\text{cm}^{-1}$ ) can also suggest the formation of  
18  $\text{R}(\text{ONO}_2)(\text{OONO}_2)$ -type compounds (Martín et al., 2002).

19 The bands at 1829–1835  $\text{cm}^{-1}$  can be assigned to the carbonyl group of the lactone with  
20 a  $-\text{ONO}_2$  group in  $\beta$  position. The effect of  $-\text{ONO}_2$  group on the carbonyl band in the  
21 lactone produce a similar displacement (to higher wavenumber) to that produced by Cl  
22 in chlorinated methylfuranones (Villanueva et al. 2007). On the other hand, Wängberg  
23 et al. (1997) associated the band found at 1829  $\text{cm}^{-1}$  with an acetyl peroxyxynitrate group  
24 [ $-\text{C}(\text{O})\text{O}_2\text{NO}_2$ ] after the reaction of pinonaldehyde with  $\text{NO}_3$ . In conclusion, based on  
25 the results obtained with Cl and OH, the band at 1829  $\text{cm}^{-1}$  together with the bands at  
26 857, 1287, 1660 could be assigned to the isomers of nitrooxy-methyl-2(5*H*)-furanone  
27 (see scheme 5).

28 The band at 1021  $\text{cm}^{-1}$  can be due to a C-OH group of the hydroxyfuranone  
29 compounds, where the carbonyl group has a negative conjugative effect and displaces  
30 the C-OH band to lower wavenumber. This band together with the absorption at 820  
31  $\text{cm}^{-1}$ , also can be also assigned to a C-O bond stretch and ring vibration of an epoxy  
32 group (Pouchert, 1989). These absorptions decreased markedly with time indicating  
33 that the possible epoxy compound formed in the reaction is thermally unstable. The

1 epoxy compound has been observed in others studies of NO<sub>3</sub> radical (Wängberg et al.,  
2 1997, Martín et al., 2002).

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

#### 6 **4. Reactions mechanism**

7 From the literature data on the reactivity of compounds with double bonds and  
8 heteroatoms in their structure, e.g. allyl acetate, propyl vinyl ether, 2-methyl-2-butenal  
9 and crotonaldehyde, it is known that these compounds undergo addition processes to the  
10 double bonds and abstraction of different H atoms in the presence of OH, generating  
11 primary and secondary carbonyl products (Magneron et al., 2002; Picquet-Varrault et al.  
12 2002; Tuazon et al., 2005; Zhou et al., 2006). Based on previous studies it is known that  
13 the reaction of NO<sub>3</sub> radicals with open and cyclic alkenes begins with the addition of the  
14 radical to the double bond, while the H-atom abstraction does not occur at all (Barnes et  
15 al., 1990; Hjorth et al., 1990; Skov et al., 1992; Jones and Ham, 2008; Rollins et al.,  
16 2009). This implies that the main products for the reaction of 3-methylfuran with OH  
17 radicals, NO<sub>3</sub> radicals and Cl atoms will come from the addition of the radical or atom  
18 to positions C2 or C5 because the most stabilized reaction intermediates are generated.  
19 H-atom abstraction is also likely to occur but this will only be a minor process. So,  
20 based on literature data, our previous work Villanueva et al. (2007, 2009) and the  
21 products indentified in this work different reaction pathways for the reaction of 3-  
22 methylfuran with Cl, OH and NO<sub>3</sub> have been proposed. Schemes 1–6.

23 In the scheme 1 the process for the generation of 2-methylbutenedial in the reaction of  
24 3-methylfuran with OH, NO<sub>3</sub> and Cl atoms is shown. 2-Methylbutenedial is a primary  
25 product that arises from the addition of the oxidant to a double bond in the C2 or C5  
26 position, with the intermediate undergoing ring opening and, depending on the nature of  
27 the substituent X (X: OH, NO<sub>3</sub>, Cl), the process will be different. For the reaction with  
28 OH, the O<sub>2</sub> abstracts the H-atom whereas in the case of Cl atoms and NO<sub>3</sub> radical the  
29 good characteristics of Cl and NO<sub>2</sub> as leaving groups mean that these groups are  
30 eliminated. This mechanism is also proposed by Bierbach et al. (1995) and Berndt et al.  
31 (1997).

1 The process for the generation of 3-methyl-2(3*H*)-furanone in the intramolecular  
2 photoisomerization of 2-methylbutenedial in the presence of VIS and UV radiation is  
3 represented in Scheme 2 (Bierbach et al., 1994). In the case where X is NO<sub>3</sub> there is no  
4 radiation but the presence of HNO<sub>3</sub> probably stabilizes the zwitterionic intermediate and  
5 thus favours the process. Bierbach et al. (1994) proposed possible reaction pathways for  
6 the formation of maleic anhydride from the OH-initiated degradation of butenedial and  
7 4-oxo-2-pentenal. Likewise, it is possible to propose a mechanism for the formation of  
8 3-methyl-2,5-furanodione from the abstraction of the aldehydic hydrogen of 2-  
9 methylbutenedial (see Scheme 3). In this case 3-methyl-2,5-furanodione would be a  
10 secondary product whose yield, together with the yield of 3-methyl-2(3*H*)-furanone,  
11 would give us the molar yield of 2-methylbutenedial. In the reaction of 3-methylfuran  
12 with OH radicals the yield of 3-methyl-2,5-furanodione is high (18%) and this indicates  
13 that 2-methylbutenedial would be a main product.

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

21 In Scheme 5 a global reaction sequence for the reaction of 3-methylfuran and X radicals  
22 (OH, NO<sub>3</sub> or Cl) has been proposed. The sequence is initiated by the addition of radical  
23 X to the carbon-carbon double bond at the 2- and/or 5-positions. In the case of the NO<sub>3</sub>  
24 radical the resulting nitrooxyalkyl radicals can either decompose to the epoxide  
25 (compounds A and/or A') plus NO<sub>2</sub> (this process typically decreases in importance as  
26 the total pressure and O<sub>2</sub> content increases) or add O<sub>2</sub> to form nitrooxyalkyl peroxy  
27 radicals (5-ONO<sub>2</sub>-3-methylfuran peroxyradical or 5-ONO<sub>2</sub>-4-methylfuran  
28 peroxyradical) (Atkinson, 1991; Atkinson, 1997). The nitrooxyalkyl peroxy radicals can  
29 (a) react with NO<sub>2</sub> to form thermally unstable peroxydinitrates [R(ONO<sub>2</sub>)(OONO<sub>2</sub>)  
30 compounds B and/or B'], (b) react with HO<sub>2</sub> radicals to form nitrooxy hydroperoxides  
31 (compounds C and/or C') and (c) react with organic peroxy (RO<sub>2</sub>) radicals. The  
32 reactions with organic peroxy radicals (including the self-reaction) proceed through a  
33 "molecular" channel, forming a nitrooxy alcohol and/or (if feasible) a nitrooxy carbonyl

1 compound (compounds D and E and/or D' and E'), and through a "radical" channel to  
2 form the nitrooxy alkoxy radicals (5-ONO<sub>2</sub>-3-methylfuran alkoxyradical or 5-ONO<sub>2</sub>-4-  
3 methylfuran alkoxyradical). The latter radicals are expected to (a) decompose to form  
4 dicarbonyl compounds as products (compounds F and/ or F'), (b) add NO<sub>2</sub> to form  
5 dinitrate compounds [R(ONO<sub>2</sub>)(ONO<sub>2</sub>) compounds G and/or G'] or (c) add molecular  
6 oxygen to form nitrooxycarbonyl compounds [compounds E and/or E', 5-nitrooxy-  
7 2(5*H*)-methylfuranone] plus the HO<sub>2</sub> radical. Our FT-IR results are consistent with  
8 Scheme 5, with evidence for the formation of the epoxide (band 820 cm<sup>-1</sup> compound A  
9 or A') nitrooxy alcohol (compound D or D') and nitrooxy carbonyl (compounds E or  
10 E'). The same sequence of reactions could be initiated by OH and Cl radicals and the  
11 products formed would be the same on changing X (ONO<sub>2</sub>) for Cl or OH. Compounds  
12 E and E' would therefore be 5-chloro-2(5*H*)-methylfuranones for the reaction of 3-  
13 methylfuran with Cl atoms and 5-hydroxy-2(5*H*)-methylfuranones for the reaction with  
14 OH radicals. However, in the reaction with Cl atoms and OH radical there was no  
15 evidence in the product analysis for the formation of compounds D/D'.

16 In conclusion the addition process with retaining configuration is the most important  
17 pathway for the reaction of 3-methylfuran with Cl atoms. This fact is corroborated by the  
18 high yields of 5-chloro-2(5*H*)-methylfuranones. In the case of the reaction with OH the  
19 dominant reaction pathway is the ring opening although it is believed that 5-hydroxy-  
20 2(5*H*)-methylfuranones (retaining configuration product) is a significant product  
21 although it could not be quantify. For the reaction with NO<sub>3</sub> although 5-nitrooxy-2(5*H*)-  
22 methylfuranones (retaining configuration products) were not identified by GC/MS and  
23 they were only tentatively assigned to certain bands in the IR spectrum, their formation  
24 is likely given the results obtained in the OH and Cl reactions. In addition, due to the low  
25 yield obtained for 2-methylbutenedial it is not possible to determine the dominant  
26 reaction pathway.

27 The presence of 5-hydroxy-4-methyl-2(5*H*)-furanone and 5-hydroxy-3-methyl-2(5*H*)-  
28 furanone as products in the reaction of 3-methylfuran with NO<sub>3</sub> and Cl was also  
29 confirmed. 5-Hydroxy-2(5*H*)-furanone was detected in the reaction of furan and  
30 alkylfurans with Cl atoms (Villanueva et al., 2007, 2009). In the case of furan, this  
31 compound was expected to be formed as a result of H-abstraction from the aromatic ring.  
32 Similarly, in the reactions of 3-methylfuran with NO<sub>3</sub> radicals and Cl atoms, 5-hydroxy-  
33 2(5*H*)-methylfuranones can only be generated by H-atom abstraction from the aromatic

1 ring in positions C2 or C5 (see Scheme 6). There are several reaction pathways for RO<sub>2</sub>  
2 + RO<sub>2</sub> radical reactions and one involves the formation of an alcohol (R–OH) and a  
3 carbonyl (RCO) co-product, as shown in Scheme 6. In this particular reaction scheme the  
4 carbonyl co-product formed is 3-methyl-2,5-furandione, which is observed  
5 experimentally. It was found in some studies that the abstraction of an H-atom from the  
6 aromatic ring in the reactions of p-xylene and 1,2,4-trimethylbenzene with OH is not  
7 favoured and the yields of the resulting methylquinones are low in comparison with the  
8 products obtained in the addition processes (Smith et al., 1999). In the case of the  
9 reaction of 3-methylfuran with NO<sub>3</sub> and Cl, 3-methyl-2,5-furanodione is formed as a co-  
10 product and therefore for Cl reactions it is likely to provide a means to estimate the yield  
11 of the 5-hydroxy-2(5*H*)-methylfuranones. Thus the yields of the 5-hydroxy-  
12 2(5*H*)-methylfuranones are expected to be ≤ 8% .

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

## 17 5. Atmospheric implications

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

$$21 \quad \tau_{\text{total}} = \frac{1}{k_X [X]} \quad (4)$$

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

28 In order to evaluate the atmospheric importance of a particular reaction it is necessary to  
29 consider the reaction mechanism and the product formation. The results of this work are  
30 consistent with the remarks and conclusions outlined below.

1 As explained in our previous studies (Villanueva et al., 2009), certain chlorinated  
2 compounds, such as the chlorinated-methylfuranones determined in this work, are  
3 formed in the atmosphere from the reaction of Cl atoms with the parent VOC.  
4 Therefore, if a chlorinated product can be identified from a particular reaction involving  
5 Cl, these products could serve as “markers” in the chemistry of Cl atoms in the  
6 troposphere.

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

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

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

24

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33



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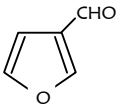
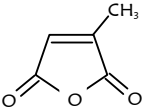
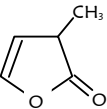
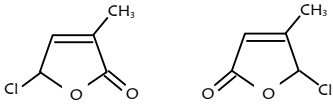
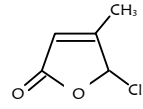
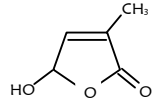
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13

1 Table 1. Rate coefficients for the reactions of 3-methylfuran with OH and NO<sub>3</sub> at atmospheric pressure and room temperature.

Reaction	Reference	$k_S/k_R^a$	$k_{298K}^b / 10^{-10}$ cm <sup>3</sup> molec. <sup>-1</sup> s <sup>-1</sup>	$\bar{k}_{298K}/10^{-10}$ cm <sup>3</sup> molec. <sup>-1</sup> s <sup>-1</sup>	Method	Bibliographic reference	
3-Methylfuran + OH	<i>trans</i> -2-Butene	1.11±0.09	0.81±0.16	1.1±0.2 <sup>c</sup>	loop/GC-MS	This work	
	5-Methylfurfural	2.27±0.08	1.16±0.06		SPME/GC-FID	This work	
	<i>trans</i> -2-Butene	1.24±0.08	0.91±0.17		FTIR	This work	
	Propene	3.6±0.3	1.08±0.17		FTIR	This work	
	2,3-Dimethyl-2-butene	-	-		0.9±0.2	FTIR	Atkinson et al., 1989
3-Methylfuran + NO <sub>3</sub>	2-Methyl-2-butene	1.36±0.02	0.13±0.01	0.13±0.02 <sup>c</sup>	Loop/GC-FID	This work	
	2-Methyl-2-butene	1.01±0.05	0.09±0.02		FTIR	This work	
	$\alpha$ -Pinene	2.0±0.1	0.116±0.009		FTIR	This work	
	2-Methyl-2-butene	-	-		0.13±0.05	GC/FID	Alvarado et al., 1996
	2,3-Dimethyl-2-butene	-	-		0.286±0.006	GC/FID	Kind et al., 1996

2 <sup>a</sup>Indicated errors are two least-squares standard deviations. <sup>b</sup>Placed on an absolute basis by use of rate constants  $k_R$  for the reactions of OH radicals with *trans*-2-butene, 5-  
3 methylfurfural and propene at 298 K of  $(7.31 \pm 1.31) \times 10^{-11}$  cm<sup>3</sup> molec.<sup>-1</sup> s<sup>-1</sup> (Edney et al., 1986),  $(5.10 \pm 0.20) \times 10^{-11}$  cm<sup>3</sup> molec.<sup>-1</sup> s<sup>-1</sup> (Bierbach et al., 1995) and  $(3.01 \pm 0.42) \times 10^{-12}$   
4 cm<sup>3</sup> molec.<sup>-1</sup> s<sup>-1</sup> (Nielsen et al., 1990), respectively; and a rate constant  $k_R$  for the reactions of NO<sub>3</sub> radicals with 2-methyl-2-butene and  $\alpha$ -Pinene of  $(9.38 \pm 3.32) \times 10^{-12}$  cm<sup>3</sup>  
5 molec.<sup>-1</sup> s<sup>-1</sup> (Atkinson, 1991) and  $(5.90 \pm 0.4) \times 10^{-12}$  (Martínez et al., 1998). <sup>c</sup>Weighted mean.

- 1 Table 2: Yields of the products (%C) detected in the reaction of 3-methylfuran with chlorine atoms at room temperature and atmospheric  
 2 pressure. The errors quoted in the table are a combination of the  $2\sigma$  statistical errors from the regression analysis and the errors from the  
 3 spectral subtraction procedure in the case of FTIR or of the calibration curve in the case of SPME-GC/FID

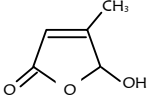
Reaction products				Molar Yield (%)	
Rt (min)	MW	name	Structure	SPME/GC-FID	FTIR
9.7	96	3-furaldehyde		$7 \pm 2^a$	$9 \pm 1^b$
9.8	98	Isomer of 3-methyl-2(5H)-furanone	$C_5H_6O_2$	$2 \pm 1^a$	-
16.7	112	3-methyl-2,5-furanodione		$8 \pm 1^a$	
11.4/11.8	98	2-methylbutenedial	$HOC-CH=C(CH_3)-CHO$	$4 \pm 1^a$	detected
18	98	3-methyl-2(3H)-furanone		$10 \pm 2^a$	-
20.9	132	5-chloro-3-methyl-2(5H)-furanone		$>16^a$	$81 \pm 9^c$
23.9	132	5-chloro-4-methyl-2(5H)-furanone		$>25^a$	
28.2	114	5-hydroxy-3-methyl-2(5H)-furanone		detected	--

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1

Table 2: continued

Reaction products				Molar Yield (%)	
Rt (min)	MW	name	Structure	SPME/GC-FID	FTIR
30.2	114	5-hydroxy-4-methyl-2(5 <i>H</i> )-furanone		detected	--
		Hydrochloric acid	HCl	--	34 ± 4 <sup>b</sup>
		Carbon monoxide	CO	--	detected

2

<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

3

1 Table 3. Atmospheric lifetimes for 3-methylfuran.

Oxidant	$k / 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\tau / \text{h}$
OH	0.91	2.46 <sup>a</sup>
NO <sub>3</sub>	0.131	1.10 <sup>b</sup>
Cl	4.2	66.14 <sup>c, d</sup>
O <sub>3</sub>	2.05x10 <sup>-7</sup>	18.22 <sup>e, f</sup>

2

3 <sup>a,b</sup>Estimated on the basis of the average concentrations in the troposphere of [OH]= 1x10<sup>6</sup>  
 4 radicals cm<sup>-3</sup> (Prinn et al., 1992) and [NO<sub>3</sub>]= 2x10<sup>7</sup> radicals cm<sup>-3</sup> (Finlayson Pitts and Pitts,  
 5 2000) respectively. <sup>c,d</sup>Estimated on the basis of kinetic rate coefficient for the reaction with  
 6 Cl atoms at 298 K (Cabañas et al., 2005) and on the basis of the average concentrations in  
 7 the troposphere of [Cl]= 1x10<sup>4</sup> atoms cm<sup>-3</sup> (Wingenter et al., 1996). <sup>e, f</sup> Estimated on the  
 8 basis of kinetic rate coefficient for the reaction with O<sub>3</sub> molecules at 298 K (Alvarado et al.,  
 9 1996) and on the basis of the average concentrations in the troposphere of [O<sub>3</sub>]= 7.4x10<sup>11</sup>  
 10 molecule cm<sup>-3</sup> (Logan, 1985).

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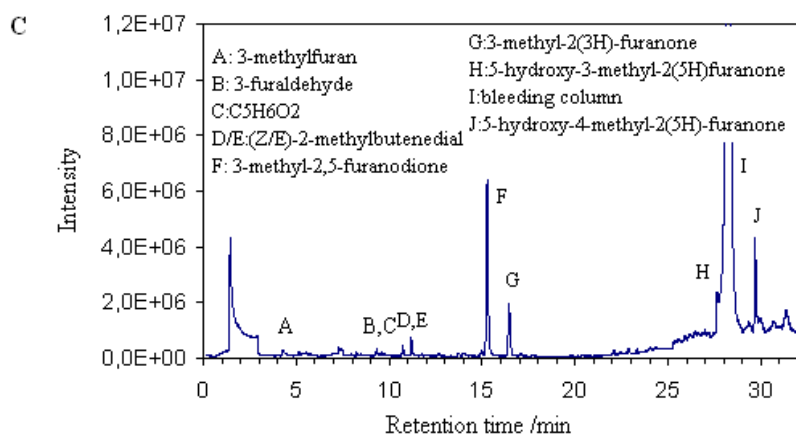
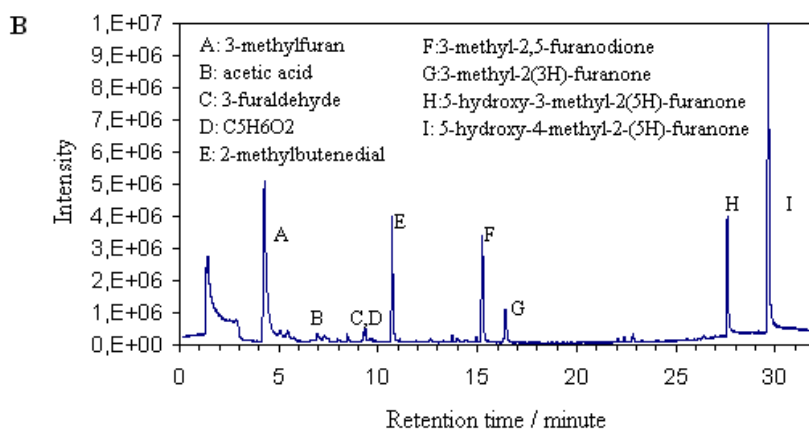
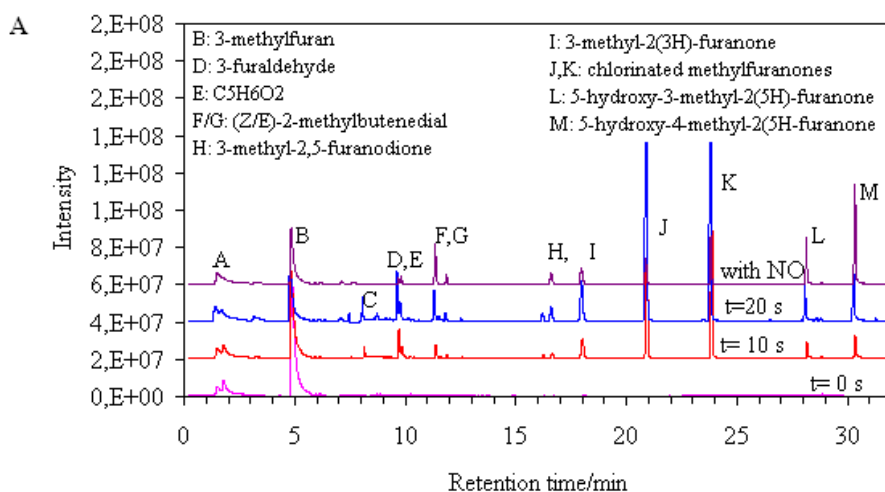
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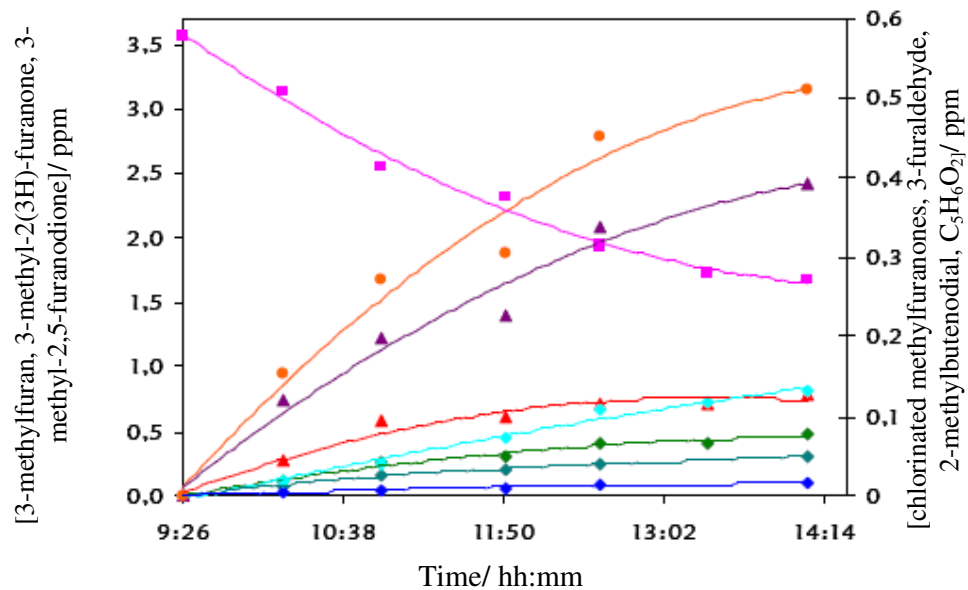
- Figure 1. Experimental chromatograms and the reaction products identified for the reactions
- of 3-methylfuran with chlorine atoms (A), hydroxyl radicals (B) and nitrate radicals (C) from
- SPME-GC/MS experiments.



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1 Figure 2. Concentration-time profiles of 3-methylfuran and products identified in the reaction of 3-  
 2 methylfuran with Cl atoms analyzed by SPME-GC-FID: (■) 3-methylfuran, (◆) 3-furaldehyde, (◆) 3-  
 3 furanone isomer, C<sub>5</sub>H<sub>6</sub>O<sub>2</sub>, (▲) 2-methylbutenedial, (◆) 3-methyl-2(3H)-furanone, (◆) 3-methyl-2,5-  
 4 furanodione, (▲) chlorinated methylfuranone (20.9 min), (●) chlorinated methylfuranone (23.9  
 5 min).

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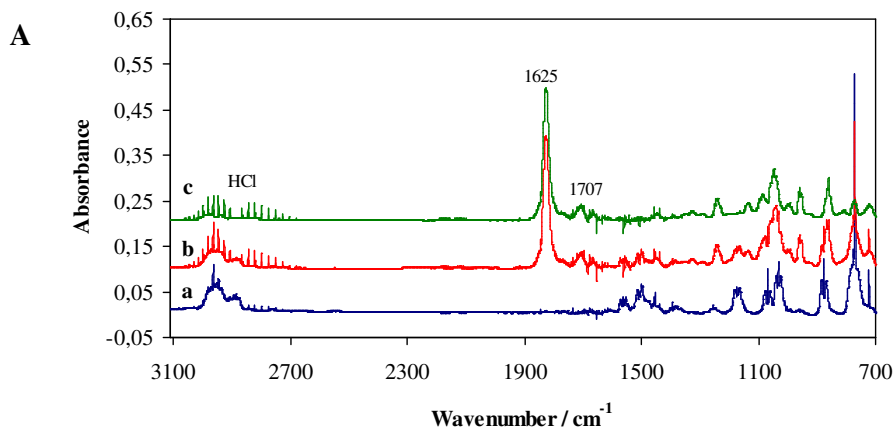
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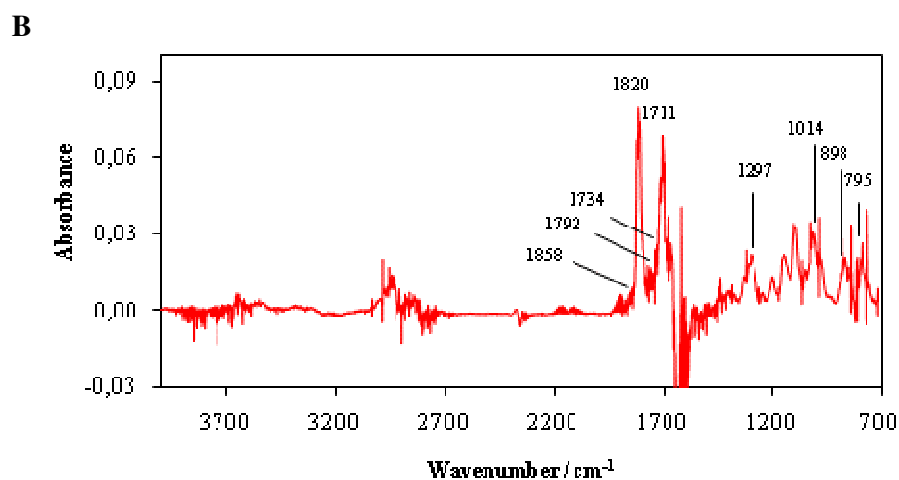
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1 Figure 3. Experimental infrared absorption spectra from the reaction of: (A) 3-methylfuran with  
2 chlorine atoms (a) before photolysis, (b) after 15 min of photolysis (c) residual spectrum from b after  
3 subtraction of 3-methylfuran, H<sub>2</sub>O with the CO<sub>2</sub> absorption zeroed; (B) 3-methylfuran with hydroxyl  
4 radical (residual spectrum of products after 8 min of reaction), (C) 3-methylfuran with nitrate radicals  
5 (residual spectrum of products after 3.4 min of reaction).



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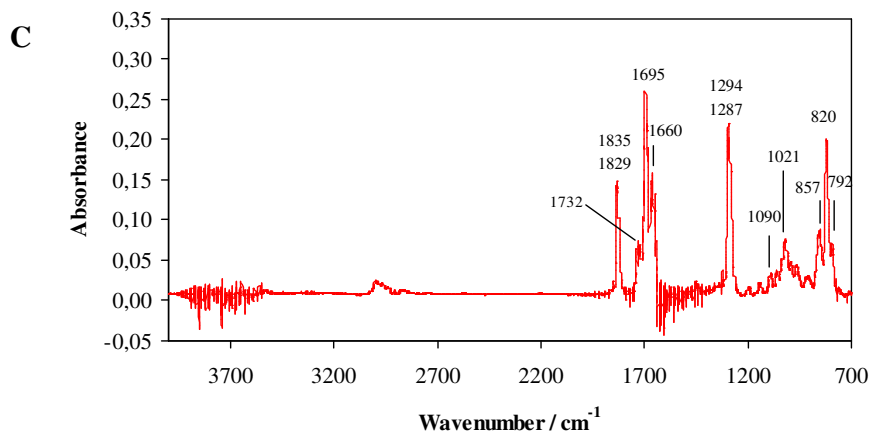
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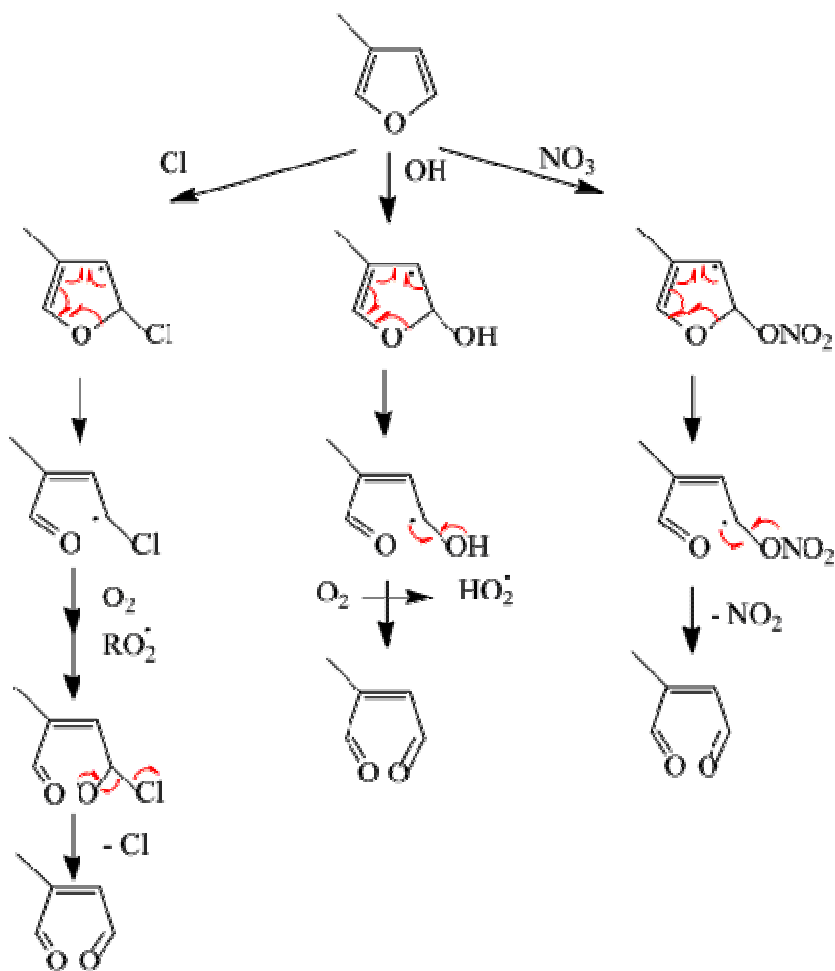
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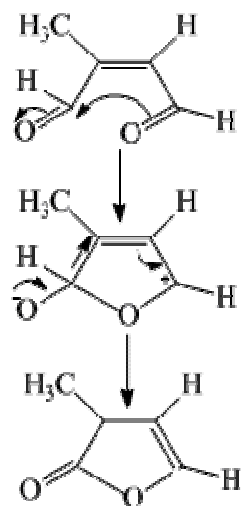


- 1 Scheme 1. Possible mechanisms for the formation of 2-methylbutenedial in the reaction of 3-
- 2 methylfuran with Cl, OH and NO<sub>3</sub>.



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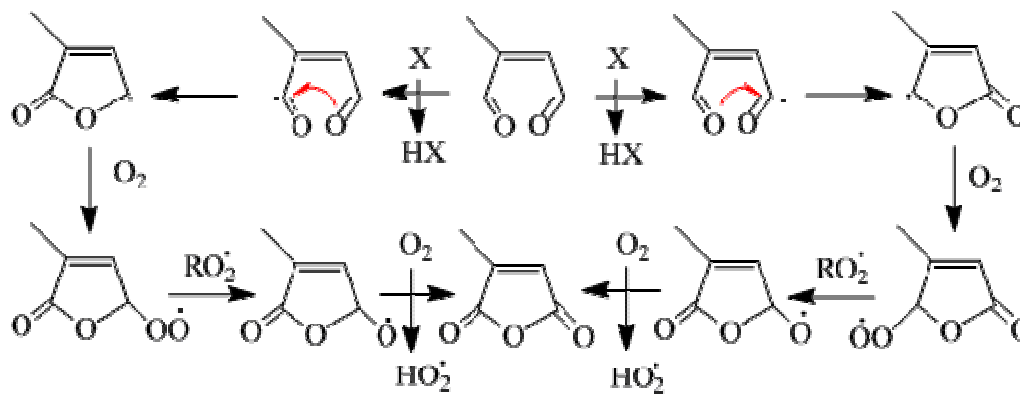
- 1 Scheme 2. Possible mechanism for the formation of 3-methyl-2(5*H*)-furanone from 2-  
2 methylbutenedial.



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- 1 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
- 2  $\text{NO}_3$ .

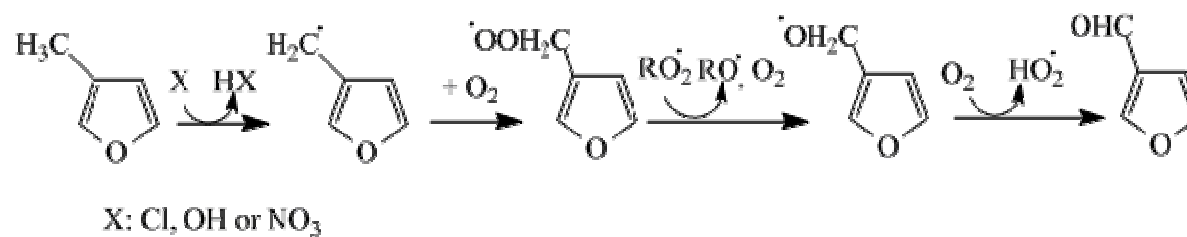


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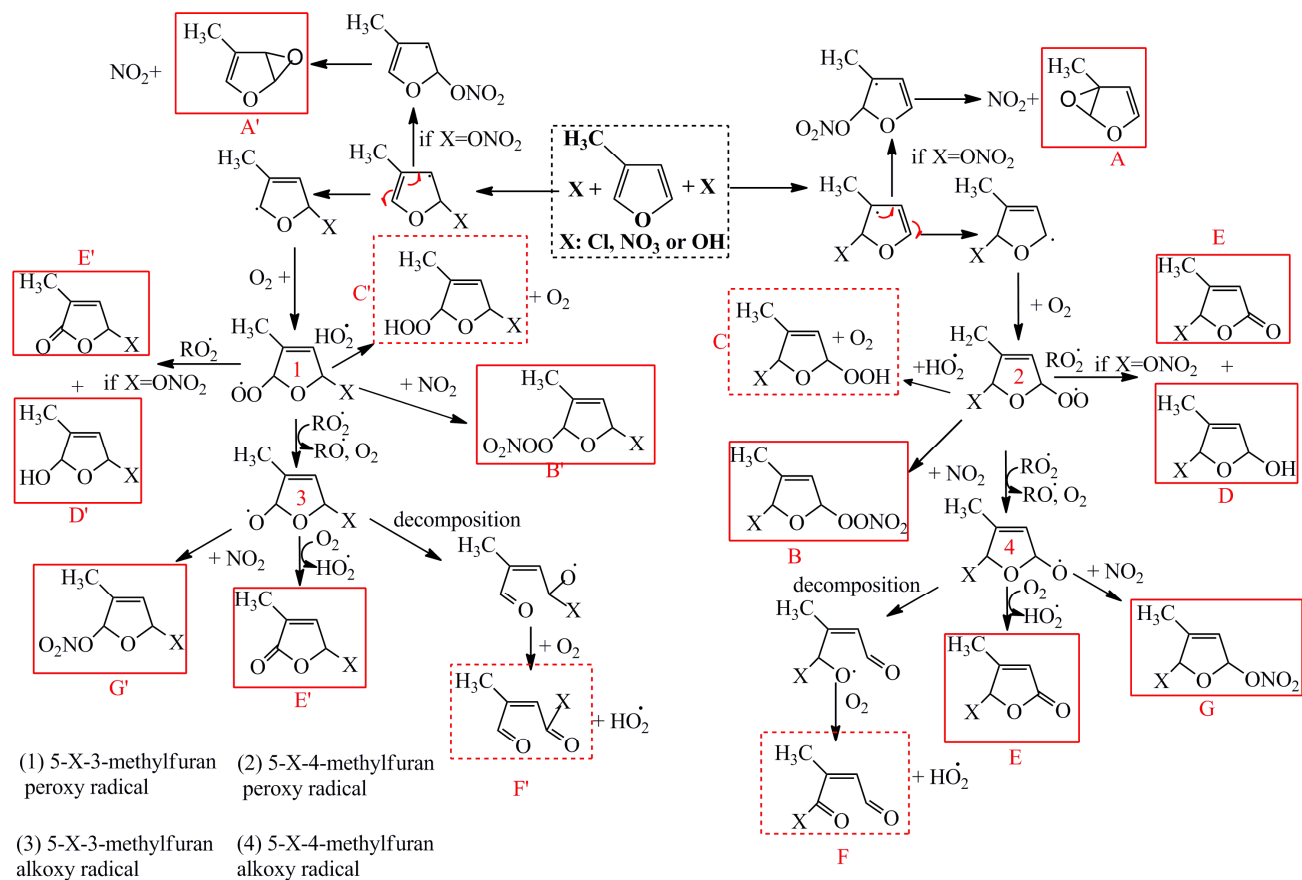
1 Scheme 4. Possible mechanisms for the formation of 3-furaldehyde in the reaction of 3-methylfuran with X, where X: Cl, OH or NO<sub>3</sub>.

2



3

- 1 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(5*H*)-furanone and 5-X-4-methyl-2(5*H*)-furanone and epoxy furan compounds. X: Cl, OH or NO<sub>3</sub>. Compounds C/C' F/F' have been not detected.
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