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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 NO₃ radicals have been determined at room temperature and atmospheric pressure (air and N₂ as bath gases), using a relative method with different experimental techniques. The absolute rate coefficients obtained for these reactions were (in units cm³ molecule⁻¹ s⁻¹): $k_{\text{OH}} = (1.13 \pm 0.22) \times 10^{-10}$ and $k_{\text{NO}_3} = (1.26 \pm 0.18) \times 10^{-11}$. These rate coefficients have been compared with those available in the literature. The products from the reaction of 3-methylfuran with OH, NO₃ and Cl atoms in the absence and in the presence of NO_x species 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 NO₃ radicals and also nitrated compounds for the reaction with NO₃ radicals. The results indicate that in all cases the main reaction path is the addition to the double bond of the aromatic ring followed by ring opening in the case of OH and NO₃ radicals. The formation of 3-furaldehyde and hydroxy-methylfuranones (in the reactions of 3-methylfuran with Cl atoms and NO₃ radicals) confirmed the H-atom abstraction from the methyl group and from the aromatic ring, respectively. This study represents the first product determination for both Cl atoms and the NO₃ 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 the degradation products of biogenics (Graedel et al., 1986; Soyer et al., 1988; Atkinson et al., 1989; Bierbach et al., 1994; Andreae and Merlet, 2001). Another important atmospheric source of 3-methylfuran

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is the photooxidation of hydrocarbons such as isoprene. In ambient air, for example, 3-methylfuran has been detected and 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).

5 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, 2006; Laothawornkitkul et al., 2009). As a result of its reactivity with
10 the OH radical, isoprene can significantly contribute to the formation of ozone in the troposphere (Atkinson and Arey, 1998). Therefore, the oxidation of isoprene is a matter of great interest in tropospheric chemistry due to its abundance and its high reactivity with atmospheric oxidants (Paulson and Seinfeld, 1992; Paulson et al., 1992; Carter and Atkinson, 1996; Stabel et al., 2004; Lee et al., 2005).

15 3-Methylfuran is also formed in the reaction of isoprene with OH 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
20 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 and this was determined using a relative technique (Atkinson
25 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 coefficients. 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).

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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
5 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 we determined rate coefficients for the reaction of OH and NO₃ radicals with 3-methylfuran in order to (i) assess the values previously
10 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 Spec-
15 troscopy) as detection techniques for the organic compounds.

We also characterized the products obtained in the reaction of 3-methylfuran with OH and NO₃ radicals and with Cl atoms 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.

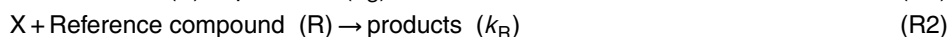
20 2 Experimental section

2.1 Kinetic study

Rate coefficients 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, were determined using a relative rate method in which the reactions of 3-methylfuran and reference compounds were monitored in the presence

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of OH or NO₃ radicals, with rate coefficients k_S and k_R , respectively:



where X is OH or NO₃.

As described in detail elsewhere (Cabañas et al., 2005), the decay of the substrate from $[S]_0$ at time $t=0$ to $[S]_t$ at time t and the simultaneous loss of the reference compound from an initial concentration of $[R]_0$ to $[R]_t$ at time t is given by Eq. (1):

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

Thus, a plot of $\ln([S]_0/[S]_t)$ vs. $(\ln[R]_0/[R]_t)$ should be a straight line passing through the origin and whose slope gives the ratio of rate coefficients k_S/k_R . Each reaction studied was measured relative to the reaction of different reference standards with oxidants X. In the case of 3-methylfuran with NO₃, 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:

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

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 NO₃ 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 NO₃ 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., 22909

2007, 2009). Only the FTIR system with a 50 L Pyrex glass vessel is described below 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 NO₃ in order to minimize the dilution effect of the additions of N₂O₅. These bags were placed inside a rectangular cage with six VIS lamps (Philips TL G13 40W/05, $\lambda_{\text{max}}=360$ nm) mounted on the walls. A system based on sample preconcentration, the solid phase microextraction technique (SPME) and a heated loop of 1 cm³ 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 °C 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 (HP 5890 Series II or 14A Shimadzu) or MS (GCMS-QP5050 Shimadzu). In all experiments a capillary column (30 m×0.32 mm id×1.0 µm film thickness, Tracsil TRB-1701, Teknokroma) of intermediate polarity was used to separate the compounds. The chromatographic conditions used for the analysis were as follows: injector, 270 °C; detector, 250 °C, the temperature program was from 40 °C (4 min) to 120 °C (17 min) at a rate of 25 °C min⁻¹.

The techniques and the reference compounds used in the reactions of 3-methylfuran with OH and NO₃ radicals are listed in Table 1.

The in situ FTIR analysis of 3-methylfuran with OH and NO₃ radicals was carried out in a 50 L Pyrex glass SATURN reaction chamber at a total pressure of approximately

760 Torr 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 (Philips TL 40W 300–460 nm, $\lambda_{\text{max}}=360$ nm) spaced evenly around the reaction chamber. The chamber was equipped with a White-type multiple-reflection mirror system 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 $4000\text{--}650\text{ cm}^{-1}$. The White system was operated 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_3ONO in air (Atkinson et al., 1981) at wavelengths of 360 nm using the VIS lamps.

The initial reactant concentrations in the reactors (in molecule cm^{-3}) were as follows: $[\text{CH}_3\text{ONO}] = (3.1\text{--}14.6) \times 10^{14}$, $[\text{NO}] = (1.7\text{--}27.5) \times 10^{14}$, $[\text{3-methylfuran}] = (1.9\text{--}8.5) \times 10^{14}$ and $[\text{reference}] = (1.7\text{--}8.7) \times 10^{14}$. In the experiments performed with LOOP/GC-MS, benzene was used as the internal standard in order to minimize the sampling and dilution errors and this was present at a concentration of $(4.4\text{--}14.8) \times 10^{14}$ molecule cm^{-3} . 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 N_2O_5 (Atkinson et al., 1984, 1988). The initial reactant concentrations in the reactors (in molecule cm^{-3}) were as follows: $[\text{3-methylfuran}] = (2.3\text{--}2.6) \times 10^{14}$, $[\text{reference}] = (2.5\text{--}2.7) \times 10^{14}$ and, in GC-FID experiments, $[\text{benzene}] = (7.2\text{--}11.7) \times 10^{13}$. During GC-FID

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experiments successive additions of N_2O_5 ($2.5 \times 10^{13}\text{--}1.1 \times 10^{14}$ molecule cm^{-3}) were performed. Sampling was carried out approximately 7 min after the addition of N_2O_5 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 the initial reactant concentrations in the reactors (in molecule cm^{-3}) were as follows: $[\text{3-methylfuran}] = (2.5\text{--}2.6) \times 10^{14}$ and $[\text{reference}] = (2.5\text{--}2.6) \times 10^{14}$, during experiments only one addition of N_2O_5 at (1.1×10^{15}) 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.

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 (Philips TUV G13, 36 W) and with provision for sampling onto a 30/50 μm SPME (DVB/CAR/PDMS) fibre. The fibre adsorption and desorption times were both 15 min, respectively, at 270°C 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°C (4 min) to 120°C (12 min) at a rate of $25^\circ\text{C min}^{-1}$, then at a rate of $10^\circ\text{C min}^{-1}$ up to 200°C (10 min). Mass spectrometry detection was performed in electronic impact mode with a detector temperature of 230°C . These experimental systems were used for the reactions of 3-methylfuran with OH and NO_3 radicals and Cl atoms; (b) in a 50 L Pyrex glass cell equipped with eight actinic fluorescent lamps (Philips TLK 40 W 300–460 nm, $\lambda_{\text{max}}=360$ nm) with in situ FTIR analysis for OH and NO_3 radicals; and (c) in a 1080 L quartz-glass cell equipped with 10 low-pressure mercury lamps (UV lamps, $\lambda_{\text{max}}=254$ nm) and 10 superactinic fluorescence lamps (Philips TL 05/40W, $320\text{ nm} < \lambda < 480\text{ nm}$, $\lambda_{\text{max}}=360$ nm) coupled with in situ FTIR analysis for Cl atoms.

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 and this was carried out using the ECN (effective carbon number) method (Scalon and Willis, 1985).

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

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

where the area is quantified from the GC/FID chromatogram and the concentration of the product is known. Sampling was performed with SMPE in the same conditions as used for the product identification experiments – in this case, however, 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 every product formed at each time t against the amounts of 3-methylfuran consumed at each time t . In some cases the plot was not linear and this means that secondary reactions involving the products took place during the reaction; e.g. wall loss, photolysis or reaction with the oxidant. In these cases, the yield was corrected by taking these reactions into account (Tuazon et al., 1986).

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2.2.1 Cl products

GC/MS, GC/ECD, GC/FID and FTIR techniques were used to identify and quantify the reaction products at 298 ± 2 K and atmospheric pressure. The experiments involving SPME GC/MS (14A SHIMADZU) and GC/FID/ECD (HP 5890 Series II) techniques were conducted in ≈ 150 L Teflon bag placed inside a chamber with four 254 nm black-lamps. Photolysis of thionyl chloride (SOCl_2) or trichloroacetyl chloride (CCl_3COCl) was used to generate atomic chlorine in irradiation steps of 8 to 10 s for SOCl_2 and 10 to 60 s for CCl_3COCl . The total photolysis time was 30–90 s for SOCl_2 and 22–720 s for CCl_3COCl with a conversion of 3-methylfuran between 21 and 94%. Cl_2 was not used as the source of Cl atoms because Cl_2 reacts with 3-methylfuran at the concentration used for this study. All experiments were carried out in the absence of NO_x and only one qualitative experiment was carried out in the presence of NO_x . The initial concentrations of the reactants in the qualitative analysis (in molecule cm^{-3} units) were: $[\text{3-methylfuran}] = (4.9\text{--}29) \times 10^{13}$, $[\text{CCl}_3\text{COCl}] = (1.4\text{--}2.4) \times 10^{14}$, $[\text{SOCl}_2] = (4.4\text{--}19) \times 10^{13}$ 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 $(7.3\text{--}14) \times 10^{13}$ and $(7.3\text{--}15) \times 10^{13}$ 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. Details of the experimental set-up can be found elsewhere (Villanueva et al., 2007). Cl atoms were generated by the photolysis of ClCOCOC and Cl_2 using 10 low-pressure mercury lamps and 8 superactinic fluorescence lamps, respectively. The total photolysis time was 11–25 min for ClCOCOC 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

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were found to be negligible in the quartz-glass reactor under the conditions used in the experimental set-up. 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: [3-methylfuran]=(1.9–2.9)×10¹³, [Cl₂]=(4.9–7.3)×10¹³ and [ClCOCOCi]=1.2×10¹³. 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: H₂O₂ photolysed from 60 s to 60 min with the 254 nm lamps in order to study the influence of NO_x on the reaction mechanisms and CH₃ONO in the presence of NO photolysed from 20 to 30 s with the 360 nm lamps in order to corroborate the presence of the products under different experimental conditions. After every photolysis a chromatogram was recorded and total photolysis times of 150–180 s and 106 min for CH₃ONO and H₂O₂ 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⁻³) were as follows: [CH₃ONO]=(1.3–2.1)×10¹⁴, [NO]=(3.2–4.4)×10¹³, [3-methylfuran]=(3.6–12)×10¹³ and [H₂O₂]=2.8×10¹⁴. In the quantitative analysis only CH₃ONO was used

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as the OH source and the concentrations (in molecule cm⁻³ units) employed were [CH₃ONO]=1.29×10¹⁴, [3-methylfuran]=3.85×10¹³ and [NO]=4.33×10¹³.

In FTIR product experiments only CH₃ONO 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⁻³) were: [CH₃ONO]=2.6×10¹⁴, [NO]=2.6×10¹⁴ and [3-methylfuran]=2.6×10¹⁴.

2.2.3 NO₃ 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⁻³) was 4.7×10¹³. Successive additions of N₂O₅ were performed corresponding to a final concentration of 2.4×10¹³ molecule cm⁻³, which resulted in an approximately 95% depletion of 3-methylfuran. In FTIR analysis the 50 L cell was used as the reactor. The initial concentrations in the cell (in molecule cm⁻³) were: [N₂O₅]=(2.8–2.9)×10¹⁴ and [3-methylfuran]=(2.4–2.9)×10¹⁴ 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%), α -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-butenic acid (Aldrich, 98%), SOCl₂ (Aldrich, +99%), CCl₃COCl (Aldrich, 99%) and ClCOCOCi (Aldrich, 98%). Gaseous products: *trans*-2-butene (Aldrich, +99%), propene (Aldrich, +99%), 2-methyl-2-butene (Aldrich, +99%), Cl₂ (Praxair, >99.8%),

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N₂ (Praxair, 99.999%), air (Praxair, 99.999%) and NO (Praxair, 99%). The following compounds were used in methylnitrite 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(5*H*)-furanones [5-hydroxy-3-methyl-(5*H*)-furanone and 5-hydroxy-4-methyl-2(5*H*)-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

Two examples of a plot of the experimental FTIR and GC/FID data according to Eqs. (1) and (2) are shown in Figs. 1 and 2 for the reaction of 3-methylfuran with OH and NO₃, respectively. Good straight-line plots were obtained. 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 kinetic 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 coefficient can be determined by the AOPWIM program from the SAR method (Aschmann and Atkinson, 1995). The value calculated in this way is 1.05×10^{-10} cm³ molecule⁻¹ s⁻¹, which is similar to the average rate coefficient value obtained in this work. The data obtained in this work can therefore be proposed as good reference data for the reaction of 3-methylfuran with OH. In relation to the reaction of 3-methylfuran with NO₃ our data are consistent with the value obtained by Alvarado et al. (1996).

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Although the values of the rate coefficients obtained from the kinetic study indicate that the first step is an electrophilic addition of the oxidant to one of the C=C bonds of 3-methylfuran, it is expected that the determination of products will allow us to establish the reaction mechanism.

According to the rate coefficients reported in Table 1 for the reaction of 3-methylfuran with OH and NO₃ radicals, together with data for Cl atoms reported by Cabañas et al. (2005), we can establish the following order of reactivity: $k_{Cl} > k_{OH} > k_{NO_3}$.

3.2 Products studies

The major challenge in identifying the reaction products from the reaction of 3-methylfuran with OH, NO₃ radicals and Cl atoms is the scarcity of commercially available standards. The identification of reaction products was carried out using the mass spectra library, the infrared spectra library, and the injection of commercially available standards [3-furaldehyde, 3-methyl-2,5-furanodione, 3-methyl-2(5*H*)-furanone, 5-hydroxy-4-methyl-2(5*H*)-furanone, crotonaldehyde, acetic acid, 2-methylpropenoic acid and 2-butenic acid], or compounds synthesized in our laboratory [2-methylbutenedial, 5-hydroxy-3-methyl-(5*H*)-furanone and 5-hydroxy-4-methyl-2(5*H*)-furanone]. 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 Fig. 3a for the oxidation of 3-methylfuran by Cl atoms in the absence of NO_x at different reaction times and in the presence of NO_x (upper chromatogram). Peaks A and C represent 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 time of authentic standards are 3-furaldehyde (peak D), 3-methyl-2,5-furanodione (peak H) and 3-methyl-2(3*H*)-furanone (peak I). Analysis of the EI mass spectrum of peak E shows the presence of the compound C₅H₆O₂ and the chemical ionization

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(Cl) 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(3*H*)-furanone or 2-methylbutenedial. Peaks F and G are assigned to (*E/Z*)-2-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(5*H*)-furanone and 5-hydroxy-4-methyl-2(5*H*)-furanone, respectively, based on EI fragmentations and the CI mass spectra, which indicate that the molecular weight is 114 (see Fig. 1 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(5*H*)-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 $C_5H_5O_2Cl$ 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(5*H*)-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(5*H*)-furanone and 5-chloro-4-methyl-2(5*H*)-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) $[HOC-CH=C(CH_3)-COOH]$ 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 Fig. 2 (in supporting information). The molecular ion peak in the CI mass spectrum (MW 132)

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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 Fig. 3a the reaction products in the absence and in the presence of NO_x 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(5*H*)-furanone.

The concentration-time dependency for the reaction products identified in the reaction of 3-methylfuran with Cl provides information about the secondary reactions that the products undergo. A slight curvature suggests the loss of some reaction products by deposition on the walls, photolysis or reaction with Cl atoms (Fig. 3 supporting information). 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_x was not performed due to the occurrence of secondary reactions that involve the formation of OH in the reaction system.

FTIR spectra recorded for different stages of the reaction of 3-methylfuran with Cl are shown in Fig. 4a: (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

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a high intensity at 1825 cm^{-1} , bands of medium intensity in the region $800\text{--}1300\text{ cm}^{-1}$ 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.

5 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

10 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.

15 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 $2695\text{--}2900\text{ cm}^{-1}$, 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

20 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 in the Wuppertal laboratory. The calculated yield of chlorinated methylfuranones is the sum of the concentrations of the two isomers as the IR spectrum is

25 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. The molar yields

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obtained for the products identified by SPME/GC-FID and FTIR are given in Table 2 together with their retention times, molecular weights and molar yields. 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

5 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

10 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 (Villanueva et al., 2007, 2009), or overestimated in the case of FTIR.

15 3.2.2 Reaction with OH radicals

In the case of FTIR experiments, and due to low signal intensity, the reaction products were only tentatively assigned in order to complete and confirm the results from SPME/GC-MS. An example of a typical chromatogram of the oxidation of 3-methylfuran by OH radicals in the presence of NO_x is shown in Fig. 3b. 3-Methylfuran is represented by peak A. The only compounds identified by the mass spectrum and by the

20 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(3*H*)-furanone (peak G) and 5-hydroxy-4-methyl-2(5*H*)-furanone (peak I). Peak H is assigned to 5-hydroxy-3-methyl-2(5*H*)-furanone by comparison with the mass spectrum and retention time of the synthesized compound. Analysis of the EI mass spectrum

25 of peak D shows the presence of a compound of formula $\text{C}_5\text{H}_6\text{O}_2$ but this was not assigned to any particular structure.

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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(3*H*)-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 H_2O_2 as a clean source of OH shows the same peaks as 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-butenic 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(5*H*)-furanone and methylsuccinic anhydride, but it is a tentative identification because they were not compared with commercial standards.

The residual FTIR spectrum for the product obtained in the oxidation of 3-methylfuran with OH radicals in the presence of NO_x is shown in Fig. 4b after subtraction of the spectra of 3-methylfuran, NO_2 , NO, HCHO, HNO_3 , HONO and CH_3ONO . Only 3-methyl-2,5-furandione 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 Fig. 4b 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. 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 . One of the most intense bands is observed at 1820 cm^{-1} and this can be assigned to a carbonyl group such as that in the hydroxy-methylfuranones. However, this assignment was not confirmed due to the low purity of the compound. 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

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that the bands at 1820 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. The results obtained by FTIR are only qualitative.

Based on the results outlined above, the main compound formed in the reaction of OH radicals with 3-methylfuran is 3-methyl-2,5-furandione. This compound could be a secondary product generated from 2-methylbutenedial, as discussed in the next section, and therefore the main products would be the isomers (*E/Z*)-2-methylbutenedial. In addition, it is reasonable to consider (based on qualitative analysis) that hydroxy-methylfuranones will be formed in significant yields in the same way as chlorinated methylfuranones are significant products from the reaction with Cl atoms.

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 Fig. 3c. 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-furandione (peak F), 3-methyl-2(3*H*)-furanone (peak G) and 5-hydroxy-4-methyl-2(5*H*)-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_2O_5 , NO_2 and HNO_3 is shown in Fig. 4c. The bands at 792 , 1294 and 1732 cm^{-1} are assigned to nitroperoxy compounds ($-\text{OONO}_2$) based on the fact that nitroperoxy compounds decompose with time (Hjorth et al., 1990; Wängberg and Ljungström, 1992) and it was easy to confirm experimentally how these bands decrease with time. The bands at 857 , 1287 ,

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1660 and 1695 cm^{-1} are assigned to nitrooxy compounds ($-\text{ONO}_2$) considering that the typical bands of this group appear at 843, 1296 and 1672 cm^{-1} (Tuazon et al., 1999). It is important to note that the band at 1695 cm^{-1} could be due to an $-\text{ONO}_2$ group next to a hydroxyl group and the band at 1660 cm^{-1} could be due to an $-\text{ONO}_2$ group next to a carbonyl group. The presence of an OH group, which has a positive conjugative effect (+K), would be expected to shift the $-\text{ONO}_2$ absorption to a higher wavenumber, likewise a CO group with negative conjugative effect (−K) would shift the $-\text{ONO}_2$ absorption to a lower wavenumber. The simultaneous presence of these two sets of bands suggests the formation of $\text{R}(\text{ONO}_2)(\text{OONO}_2)$ -type compounds (Martín et al., 2002).

Compounds such as 3-methyl-2,5-furanodione, 3-methyl-2(5*H*)-furanone and 5-hydroxy-4-methyl-2(5*H*)-furanone were not found in the FTIR analysis, probably because the bands were overlapped by the bands of the major products. However, some bands can be assigned in order to confirm the presence of certain functional groups – including the band at $1829\text{--}1835\text{ cm}^{-1}$, which could belong to a carbonyl group. As explained for chlorinated methylfuranones in the reaction of 3-methylfuran with Cl atoms, the presence of $-\text{ONO}_2$ in the β position (with a positive conjugative effect) would be expected to shift the carbonyl absorption (in the lactone group) to a higher wavenumber. On the other hand, Wängberg et al. (1997) associated the band found at 1829 cm^{-1} with an acetyl peroxyxynitrate group [$-\text{C}(\text{O})\text{O}_2\text{NO}_2$] after the reaction of pinonaldehyde with NO_3 . This supports the proposal that a group with a positive conjugative effect, such as $-\text{ONO}_2$, leads to a displacement of the band to higher wavenumber. Therefore, 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(5*H*)-furanone. The band at 1021 cm^{-1} could 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. The bands at 1061 and 1090 cm^{-1} could be due to hydroxynitrate compounds where the nitrate group has a positive conjugative effect and displaces the C–OH band to higher wavenumber. The

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band at 820 cm^{-1} has a high intensity and could correspond to an epoxy group, the presence of which has been demonstrated after the addition process of the NO_3 radical to the double bonds in alkenes (Wängberg et al., 1997; Martín et al., 2002).

4 Products study conclusions

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 NO_3 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, NO_3 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.

Nevertheless, it is necessary to consider other compounds present in the reaction mixture, such as NO_x compounds that arise from the precursors of OH (CH_3ONO) and NO_3 (N_2O_5). These compounds could also react with the intermediate radicals.

The literature data and the reaction products identified in this work allowed us to establish the mechanisms that lead to these compounds. The possible reaction pathways for the reaction of 3-methylfuran with Cl, OH and NO_3 are shown in Schemes 1–6 and these are based on our experimental data and the results of Villanueva et al. (2007, 2009).

Firstly, it must be considered that in the presence of OH and NO₃ the alkoxy radicals could be formed from the reactions RO₂+RO₂ and RO₂+NO.

Butenedial was detected as the main product in the reactions of furan with OH by Bierbach et al. (1995) and Gómez Álvarez et al. (2009), with yields of 70 and 99%, respectively. Butenedial is also the main product in the reaction of furan with NO₃ and is formed in 96% yield (Berndt et al., 1997). Although this compound is detected in the reaction of furan with Cl in the absence of NO the yield is lower (11% and 1.6% each isomer), a finding that supports the existence of processes other than the ring opening after addition of the oxidant (Villanueva et al., 2007). The process for the generation of 2-methylbutenedial in the reaction of 3-methylfuran with OH, NO₃ and Cl atoms is represented in Scheme 1. 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. In the case where X is Cl the addition of O₂ and the elimination of the Cl atom occur. In the reaction involving OH, the O₂ abstracts the H-atom whereas in the case of NO₃ the good characteristics of NO₂ as a leaving group mean that this group is eliminated. The low yields of 2-methylbutenedial could be due to the occurrence of secondary reactions to form products such as 3-methyl-2(3*H*)-furanone and 3-methyl-2,5-furanodione – especially in the reactions involving OH radicals. The process for the generation of 3-methyl-2(3*H*)-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 NO₃ there is no radiation but the presence of HNO₃ 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

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yield of 3-methyl-2(3*H*)-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. As mentioned above, Bierbach et al. (1995) quantified high yields of butenedial and 4-oxo-2-pentenal (approximately 70% and 70%, respectively) in the chemical degradation of furan and 2-methylfuran with OH radicals. Gómez Álvarez et al. (2009) studied the degradation of 3-methylfuran with OH radicals and reported that the main pathway was ring-opening leading to 2-methylbutenedial, which was quantified at (75±23) ppb [i.e. a yield of (83±33)%].

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). A possible reaction pathway for the formation of 3-furaldehyde in the reaction of 3-methylfuran with OH, NO₃ and Cl as the primary product is represented in Scheme 4. Evidence for this process was not reported in the study of Gómez Álvarez et al. (2009). However, on the basis of the yield obtained this process is not as favoured as others.

The reaction sequences proposed for the reaction of 3-methylfuran and X radicals (OH, NO₃ or Cl) are shown in Scheme 5. 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 NO₃ radical the resulting nitrooxyalkyl radicals can either decompose to the epoxide (compounds A and/or A') plus NO₂ (this process typically decreases in importance as the total pressure and O₂ content increases) or add O₂ to form nitrooxyalkyl peroxy radicals (5-ONO₂-3-methylfuran peroxyradical or 5-ONO₂-4-methylfuran peroxyradical) (Atkinson, 1991; Atkinson, 1997). The nitrooxyalkyl peroxy radicals can (a) react with NO₂ to form thermally unstable peroxydinitrates [R(ONO₂)(OONO₂) compounds B and/or B'], (b) react with HO₂ radicals to form nitrooxy hydroperoxides (compounds C and/or C') and (c) react with organic peroxy (RO₂) 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 com-

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pound (compounds D and E and/or D' and E'), and through a "radical" channel to form the nitrooxy alkoxy radicals (5-ONO₂-3-methylfuran alkoxyradical or 5-ONO₂-4-methylfuran alkoxyradical). The latter radicals are expected to (a) decompose to form dicarbonyl compounds as products (compounds F and/or F'), (b) add NO₂ to form dinitrate compounds [R(ONO₂)(ONO₂) 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 HO₂ 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') observed and with the nitrooxy alcohol (compound D or D'), nitrooxy carbonyl (compounds E or E') and nitrooxy hydroperoxide species (compound C or C') accounting for the remainder of the products. The same sequence of reactions could be initiated by OH and Cl radicals and the products formed would be the same on changing X (ONO₂) 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 there was no evidence in the product analysis for the formation of compounds D/D', C/C' and F/F'.

The addition process in the reaction of 3-methylfuran with X is the most favoured of all the possible mechanisms (Berndt et al., 1997; Martín et al., 2002; Jones et al., 2008). This fact is corroborated by the yields of 5-chloro-2(5H)-methylfuranones that are the major products in the reaction of 3-methylfuran with Cl. Although it was not possible to quantify 5-hydroxy-2(5H)-methylfuranones, we believe that this is a significant product in the reaction of 3-methylfuran with OH radicals along with 2-methylbutenedial. 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. Likewise, although 5-nitrooxy-

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2(5H)-methylfuranones were not identified by GC/MS and it was only tentatively assigned to certain bands in the IR spectrum, the formation of this compound is likely given the results obtained in the OH and Cl reactions.

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 NO₃ 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 NO₃ 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 RO₂+RO₂ 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. In the case of the OH radical, the formation of hydroxy-2(5H)-methylfuranones could be explained by the addition of the OH radical to a double bond in positions C2 or C5 of the aromatic ring, as explained above. It was not possible to quantify the 5-hydroxy-2(5H)-methylfuranones due to the low purity levels of the commercial standard and the synthesized sample. 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 NO₃ 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(5H)-methylfuranones. Thus the yields of the 5-hydroxy-2(5H)-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.,

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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, NO₃, Cl and O₃ by applying Eq. (4)

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

and the average concentrations of these compounds in the troposphere: [OH]=1×10⁶ radicals cm⁻³ (Prinn et al., 1992), [NO₃]=2×10⁷ radicals cm⁻³ (Finlayson-Pitts and Pitts, 2000), [Cl]=1×10⁴ atoms cm⁻³ (Wingenter et al., 1996) and [O₃]=7.4×10¹¹ molecule cm⁻³ (Logan, 1985). As shown in Table 3, OH and NO₃ radicals are the most important sinks for 3-methylfuran at daytime and night-time, respectively, with lifetime values of 2.5 and 1 h.

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 NO₃ 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

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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.

Supplementary material related to this article is available online at:

<http://www.atmos-chem-phys-discuss.net/10/22905/2010/>

[acpd-10-22905-2010-supplement.pdf](#).

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References

Alvarado, A., Atkinson, R., and Arey, J.: Kinetics of the gas-phase reactions of NO₃ radicals and O₃ with 3-methylfuran and the OH radical yield from the O₃ reaction, *Int. J. Chem. Kinet.*, 28(12), 905–909, 1996.

22932

- Andreae, M. O. and Merlet, P.: Emission of trace gases and aerosols from biomass burning, *Global Biogeochem. Cy.*, 15(4), 955–966, 2001.
- Aschmann, S. M. and Atkinson, R.: Rate constants for the gas-phase reactions of alkanes with Cl atoms at 296 ± 2 K, *Int. J. Chem. Kinet.*, 27(6), 613–622, 1995.
- 5 Atkinson, R., Carter, W. P. L., Winer, A. M., and Pitts Jr., J. N.: An experimental protocol for the determination of OH radical rate constants with organics using methyl nitrite as an OH radical source, *JAPCA J. Air Waste Ma.*, 31, 215–290, 1981.
- Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M., and Pitts Jr., J. N.: Rate constants for the gas phase reactions of NO_3 radicals with a series of organic in air at 298 ± 1 K, *J. Phys. Chem.*, 88, 1210–1215, 1984.
- 10 Atkinson, R., Aschmann, S. M., and Pitts Jr., J. N.: Rate constants for the gas-phase reactions of the nitrate radical with a series of organic compounds at 296 ± 2 K, *J. Phys. Chem.*, 92, 3454–3457, 1988.
- Atkinson, R., Aschmann, S. A., Tuazon, E. C., Arey, J., and Zielinska, B.: Formation of 3-methylfuran from the gas-phase reaction of OH radicals with isoprene and the rate constant for its reaction with the OH radical, *Int. J. Chem. Kinet.*, 21, 593–604, 1989.
- 15 Atkinson, R.: Kinetics and mechanisms of the gas-phase reactions of the NO_3 radical with organic compounds, *J. Phys. Chem. Ref. Data*, 20, 459–507, 1991.
- Atkinson, R.: Gas-phase tropospheric chemistry of volatile organic compounds: 1. alkanes and alkenes, *J. Phys. Chem. Ref. Data*, 26, 215–290, 1997a.
- 20 Atkinson, R. and Arey, J.: Atmospheric chemistry of biogenic organic compounds, *Acc. Chem. Res.*, 31, 574–583, 1998.
- Barnes, I., Bastian, V., Becker, K. H., and Tong, Z.: Kinetics and products of the reactions of NO_3 with monoalkenes, dialkenes, and monoterpenes, *J. Phys. Chem.*, 94, 2413–2419, 1990.
- 25 Berndt, T., Böge, O., and Rolle, W.: Products of the gas-phase reactions of NO_3 radicals with furan and tetramethylfuran, *Environ. Sci. Technol.*, 31, 1157–1162, 1997.
- Bierbach, A., Barnes, I., and Becker, K. H.: Product and kinetic study of the OH-initiated gas-phase oxidation of furan, 2-methylfuran and furanaldehydes at 300 K, *Atmos. Environ.*, 29(19), 2651–2660, 1995.
- 30 Bierbach, A., Barnes, I., Becker, K. H., and Wiesen, E.: Atmospheric chemistry of unsaturated carbonyls: butenedial, 4-oxo-2-pentenal, 3-hexene-2,5-dione, maleic anhydride, 3H-furan-2-one, and 5-methyl-3H-furan-2-one, *Environ. Sci. Technol.*, 28, 715–729, 1994.

22933

- Cabañas, B., Tapia, A., Villanueva, F., Salgado, S., Monedero, E., and Martín, P.: Kinetic study of 2-furaldehyde, 3-furaldehyde and 5-methyl-2-furaldehyde reactions initiated by Cl atoms, *Int. J. Chem. Kinet.*, 40(10), 670–678, 2008.
- Cabañas, B., Villanueva, F., Martín, P., Baeza, M. T., Salgado, S., and Jiménez, E.: Study of reaction processes of furan and some furan derivatives initiated by Cl atoms, *Atmos. Environ.*, 39, 1935–1944, 2005.
- 5 Carter, W. P. L.: Development of ozone reactivity scales for volatile organic compounds, *J. Air Waste Manage.*, 44, 881–899, 1994a.
- Carter, W. P. and Atkinson, R.: Development and evaluation of a detailed mechanism for the atmospheric reactions of isoprene and NO_x , *Int. J. Chem. Kinet.*, 28, 497–530, 1996.
- 10 Carter, W. P. L.: Development of the SAPRC-07 Chemical Mechanism and Updated Ozone Reactivity Scales. Final report to the California Air Resources, available at: www.cert.ucr.edu/~carter/SAPRC, 2010a.
- Carter, W. P. L.: Development of the SAPRC-07 chemical mechanism, *Atmos. Environ.*, doi:10.1016/j.atmosenv.2010.01.026, in press, 2010b.
- 15 Edney, E. O., Kleindienst, T. E., and Corse, E. W.: Room temperature rate constants for the reaction of OH with selected chlorinated and oxygenated hydrocarbons, *Int. J. Chem. Kinet.*, 18(12), 1355–1371, 1986.
- Finlayson-Pitts, B. J. and Pitts, J. N.: *Upper and lower atmosphere*, San Diego, Academic Press, 2000.
- 20 Gómez Álvarez, E., Borrás, E., Viidanoja, J., and Hjorth, J.: Unsaturated dicarbonyl products from the OH-initiated photo-oxidation of furan, 2-methylfuran and 3-methylfuran, *Atmos. Environ.*, 43, 1603–1612, 2009.
- Graedel, T. E., Hawkings, D. T., and Claxton, L. D.: *Atmospheric Chemical Compounds: Sources, Occurrence, and Bioassay*, Academic Press, New York, 1986.
- 25 Gu, C.-L., Rynard, C. M., Hendry, D. G. and Mill, T.: Hydroxyl radical oxidation of isoprene, *Environ. Sci. Technol.*, 29, 2467–2469, 1995.
- Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmos. Chem. Phys.*, 6, 3181–3210, doi:10.5194/acp-6-3181-2006, 2006.
- 30 Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmer-

22934

- man, P.: A global model of natural organic compound emissions, *J. Geophys. Res.*, 100, 8873–8892, 1995.
- Hjorth, J., Lobse, C., Nielsen, C. J., Skov, H., and Restelli, G.: Products and mechanisms of the gas-phase reactions between NO_3 and a series of alkenes, *J. Phys. Chem.*, 94, 7494–7500, 1990.
- Jones, B. T. and Ham, J. E.: α -Terpineol reactions with the nitrate radical: rate constant and gas-phase products, *Atmos. Environ.*, 42, 6689–6698, 2008.
- Kind, I., Berndt, T., Boge, O., and Rolle, W.: Gas-phase rate constants for the reaction of NO_3 radicals with furan and methyl-substituted furans, *Chem. Phys. Lett.*, 256, 679–683, 1996.
- Kumar, P. and Pandey, R. K.: An efficient synthesis of 5-hydroxy-2(5H)-furanone, *Green Chem.*, 2(1), 29–32, 2000.
- Laothawornkitkul, J., Taylor, J. E., Paul, N. D., and Hewitt, C. N.: Biogenic volatile organic compounds in the Earth system, *New Phytol.*, 183, 27–51, 2009.
- Lee, W., Baasandorj, M., Stevens, P. S., and Hites, R. A.: Monitoring OH-initiated oxidation kinetics of isoprene and its products. Products using online mass spectrometry, *J. Phys. Chem. A*, 109(21), 4728–4735, 2005.
- Logan, J. A.: Tropospheric ozone-seasonal behaviour, trends, and anthropogenic influence, *J. Geophys. Res.*, 90, 463–482, 1985.
- Magneron, I., Thévenet, R., Mellouki, A., and Le Bras, G.: A study of the photolysis and OH-initiated oxidation of acrolein and trans-crotonaldehyde, *J. Phys. Chem. A*, 106, 2526–2537, 2002.
- Martín, M. P., Tuazon, E. C., Aschmann, S. M., Arey, J., and Atkinson, R.: Formation and atmospheric reactions of 4,5-dihydro-2-methylfuran, *J. Phys. Chem. A*, 106, 11492–11501, 2002.
- Martínez, E., Cabanas, B., Aranda, A., and Martín, P.: Kinetics of the reactions of NO_3 radical with selected monoterpenes: a temperature dependence study, *Environ. Sci. Technol.*, 32(23), 3730–3734, 1998.
- Montzka, S. A., Trainer, M., Angevine, W. M., and Fehsenfeld, F. C.: Measurements of 3-methylfuran, methyl vinyl ketone, and methacrolein at a rural forested site in the southeastern United States, *J. Geophys. Res.*, 100(D6), 11393–11401, doi:10.1029/95JD01132, 1995.
- Muller, J. F.: Geographical distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gases, *J. Geophys. Res.*, 97, 3787–3804, 1992.
- Nielsen, O. J., Jorgensen, O., Donlon, M., Sidebottom, H. W., O'Farrell, D. J., and Treacy, J.:

22935

- Rate constants for the gas-phase reactions of OH radicals with nitroethene, 3-nitropropene and 1-nitrocyclohexene at 298 K and 1 atm, *Chem. Phys. Lett.*, 168(3–4), 319–323, 1990.
- Nozière, B., Lesclaux, R., Hurley, M. D., Dearth, M. A., and Wallington, T. J.: A kinetic and mechanistic study of the self-reaction and reaction with HO_2 of the benzylperoxy radical, *J. Phys. Chem.*, 98, 2864–2873, 1994.
- Paulson, S. E. and Seinfeld, J. E.: Development and evaluation of photooxidation mechanism for isoprene, *J. Geophys. Res.*, 97, 20703–20717, 1992.
- Paulson, S. E., Flagan, R. C., and Seinfeld, J. H.: Atmospheric photooxidation of isoprene part I: the hydroxyl radical and ground-state atomic oxygen reactions, *Int. J. Chem. Kinet.*, 24, 79–102, 1992.
- Picquet-Varrault, B., Doussin, J. F., Durrand-Jolibois, R., Pirali, O., and Carlier, P.: Kinetic and mechanistic study of the atmospheric oxidation by OH radicals of allyl acetate, *Environ. Sci. Technol.*, 36, 4081–4086, 2002.
- Prinn, R., Cunnold, D., Simmonds, P., Alyea, F., Boldi, R., Crawford, A., Froser, P., Gutzler, D., Hartley, R., Rosen, R., and Rasmussen, R.: Global average concentration and trend for hydroxyl radicals deduced from ALE/GAGE trichloroethane (methyl chloroform) data for 1978–1990, *J. Geophys. Res.*, 97, 2445–2461, 1992.
- Rollins, A. W., Kiendler-Scharr, A., Fry, J. L., Brauers, T., Brown, S. S., Dorn, H. P., Dubé, W. P., Fuchs, H., Mensah, A., Mentel, T. F., Rohrer, F., Tillmann, R., Wegener, R., Wooldridge, P. J., and Cohen, R. C.: Isoprene oxidation by nitrate radical: alkyl nitrate and secondary organic aerosol yields, *Atmos. Chem. Phys.*, 9, 6685–6703, doi:10.5194/acp-9-6685-2009, 2009.
- Ruppert, L. and Becker, K. H.: A product study of the OH radical-initiated oxidation of isoprene: formation of C_5 -unsaturated diols, *Atmos. Environ.*, 34(10), 1529–1542, 2000.
- Scalon, T. J. and Willis, D. E.: Calculation of flame ionization detector response factors using effective number concept, *J. Chromatogr. Sci.*, 23, 333–340, 1985.
- Skov, H., Hjorth, J., Lohse, C., Jensen, N. R., and Restelli, G.: Products and mechanisms of the reactions of the nitrate radical (NO_3) with isoprene, 1,3-butadiene and 2,3-dimethyl-1,3-butadiene in air, *Atmos. Environ.*, 26A(15), 2771–2783, 1992.
- Smith, D. F., Kleindienst, T. E., and McIver, C. D.: Primary product distributions from the reaction of OH with *m*-, *p*-xylene, 1,2,3- and 1,3,5-trimethylbenzene, *J. Atmos. Chem.*, 34, 339–364, 1999.
- Soyer, N., Hyvrard, F., Bruneau, C., and Brault, A.: In: *Pyrolysis Oils from Biomass*, edited by: Soltes, E. J. and Milne, T. A., ACS Symposium Series 376, ACS, Washington, DC, 220–227,

22936

- 1988.
- Stabel, J. R., Johnson, M. S., and Langer, S.: Rate coefficients for the gas-phase reaction of isoprene with NO_3 and NO_2 , *Int. J. Chem. Kinet.*, 37, 57–65, 2004.
- 5 Tuazon, E. C., Mac Leod, H., Atkinson, R., and Carter, W. P. L.: α -Dicarbonyl yields from the NO_x -air photooxidations of a series of aromatic hydrocarbons in air, *Environ. Sci. Technol.*, 20, 383–387, 1986.
- Tuazon, E. C. and Atkinson, R. J.: A product study of the gas-phase reaction of isoprene with the OH radical in the presence of NO_x , *Int. J. Chem. Kinet.*, 22, 1221–1236, 1990.
- 10 Tuazon, E. C., Alvarado, A., Aschmann, S., Atkinson, R., and Arey, J.: Products of the gas-phase reactions of 1,3-butadiene with OH and NO_3 radicals, *Environ. Sci. Technol.*, 33, 3586–3595, 1999.
- Tuazon, E. C., Aschmann, S. M., Nishino, N., Arey, J., and Atkinson, R.: Kinetics and products of the OH radical-initiated reaction of 3-methyl-2-butenal, *Phys. Chem. Chem. Phys.*, 7, 2298–2304, 2005.
- 15 Villanueva, F., Barnes, I., Monedero, E., Salgado, S., Gómez, M. V., and Martín, P.: Primary product distribution from the Cl-atom initiated atmospheric degradation of furan: environmental implications, *Atmos. Environ.*, 41(38), 8796–8810, 2007.
- Villanueva, F., Cabañas, B., Monedero, E., Salgado, S., Bejan, I., Martín, P.: Atmospheric degradation of alkylfurans with chlorine atoms: product and mechanistic study, *Atmos. Environ.*, 43(17), 2804–2813, 2009.
- 20 Wang, L., Arey, J., and Atkinson, R.: Reactions of chlorine atoms with a series of aromatic hydrocarbons, *Environ. Sci. Technol.*, 39, 5302–5310, 2005.
- Wängberg, I. and Ljungström, E.: FTIR studies of reactions between the NO_3 radical and cycloalkenes. Chemical Mechanisms describing tropospheric processes, *Air Pollut. Res.*, 45, 113–117, 1992.
- 25 Wängberg, I., Barnes, I., and Becker, K. H.: Product and mechanistic study of the reaction of NO_3 radicals with α -pinene, *Environ. Sci. Technol.*, 31, 2130–2135, 1997.
- Wingenter, O. W., Kubo, M. K., Blake, N. J., Smith Jr., T. W., Blake, D. R., and Rowland, F. S.: Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine, and vertical mixing obtained during Lagrangian flights, *J. Geophys. Res.*, 101, 4331–4340, 1996.
- 30 Zhang, W., Du, B., Mu, L., and Feng, C.: Mechanism for the gas-phase reaction between OH and 3-methylfuran: Mechanism for the gas-phase reaction between OH and 3-methylfuran:

22937

- a theoretical study, *Int. J. Quant. Chem.*, 108, 1232–1238, 2008.
- Zhou, S., Barnes, I., Zhu, T., Bejan, I., and Benter, T.: Kinetic study of the gas-phase reactions of OH and NO_3 radicals and O_3 with selected vinyl ethers, *J. Phys. Chem. A*, 110(23), 7386–7392, 2006.

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

Reaction	Reference	k_S/k_R^a	$k_{298K}^b/10^{-10}$ cm ³ molecule ⁻¹ s ⁻¹	$\bar{k}_{298K}/10^{-10}$ cm ³ molecule ⁻¹ s ⁻¹	Method	Bibliographic reference
3-Methylfuran+OH	<i>trans</i> -2-Butene	1.11±0.09	0.81±0.16	1.1±0.2 ^c	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	–	–		FTIR	Atkinson et al., 1989
3-Methylfuran+NO ₃	2-Methyl-2-butene	1.36±0.02	0.13±0.01	0.13±0.02 ^c	Loop/GC-FID	This work
	2-Methyl-2-butene	1.01±0.05	0.09±0.02		FTIR	This work
	α -Pinene	2.0±0.1	0.116±0.009		FTIR	This work
	2-Methyl-2-butene	–	–		GC/FID	Alvarado et al., 1996
	2,3-Dimethyl-2-butene	–	–		GC/FID	Kind et al., 1996

^a Indicated errors are two least-squares standard deviations.

^b Placed 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 $(7.31\pm1.31)\times10^{-11}$ cm³ molecule⁻¹ s⁻¹ (Edney et al., 1986), $(5.10\pm0.20)\times10^{-11}$ cm³ molecule⁻¹ s⁻¹ (Bierbach et al., 1995) and $(3.01\pm0.42)\times10^{-12}$ cm³ molecule⁻¹ s⁻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 $(9.38\pm3.32)\times10^{-12}$ cm³ molecule⁻¹ s⁻¹ (Atkinson, 1991) and $(5.90\pm0.4)\times10^{-12}$ (Martínez et al., 1998).

^c Weighted mean.

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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 2 σ 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.

Reaction products				Molar Yield (%)	
Rt (min)	MW	name	Structure	SPME/GC-FID	FTIR
9.7	96	3-furaldehyde		7 ± 2 ^a	9 ± 1 ^b
9.8	98	Isomer of 3-methyl-2(5H)-furanone	C ₅ H ₆ O ₂	2 ± 1 ^a	–
16.7	112	3-methyl-2,5-furandione		8 ± 1 ^a	–
11.4/11.8	98	2-methylbutenedial	HOC-CH=C(CH ₃)-CHO	4 ± 1 ^a	detected
18	98	3-methyl-2(3H)-furanone		10 ± 2 ^a	–
20.9	132	5-chloro-3-methyl-2(5H)-furanone		>16 ^a	81 ± 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	–

22940

Table 2. Continued.

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

^a Average of 5 experiments with UV lamps^b Only 1 experiment with VIS lamps^c Average of 8 experiments with UV and VIS lamps

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Table 3. Atmospheric lifetimes for 3-methylfuran.

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

^{a,b} Estimated on the basis of the average concentrations in the troposphere of [OH]= 1×10^6 radicals cm⁻³ (Prinn et al., 1992) and [NO₃]= 2×10^7 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]= 1×10^4 atoms cm⁻³ (Wingenter et al., 1996).^{e,f} Estimated on the basis of kinetic rate coefficient for the reaction with O₃ molecules at 298 K (Alvarado et al., 1996) and on the basis of the average concentrations in the troposphere of [O₃]= 7.4×10^{11} molecule cm⁻³ (Logan, 1985).

22942

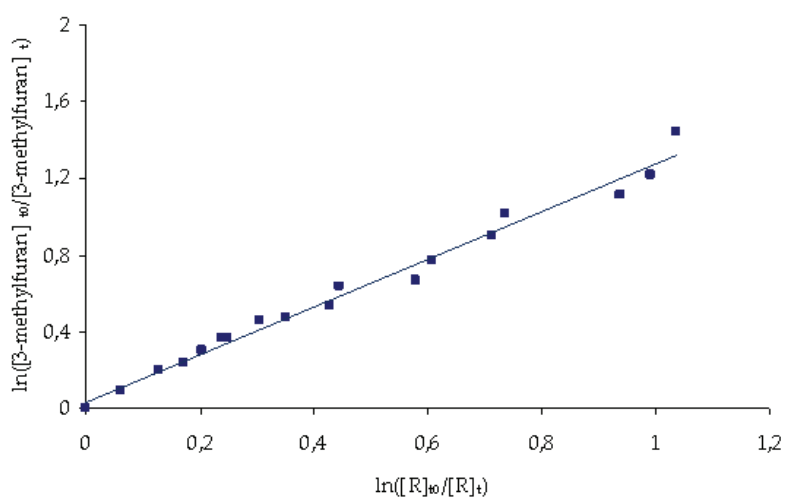


Fig. 1. Plot of Eq. (1) for the reactions of OH radicals with 3-methylfuran, with *trans*-2-butene as the reference compound.

22943

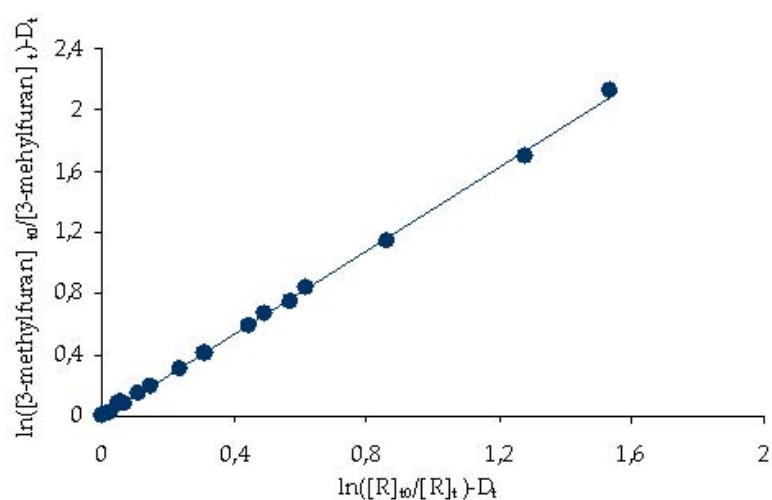


Fig. 2. Plot of Eq. (2) for the reactions of NO₃ radicals with 3-methylfuran, with 2-methyl-2-butene as the reference compound.

22944

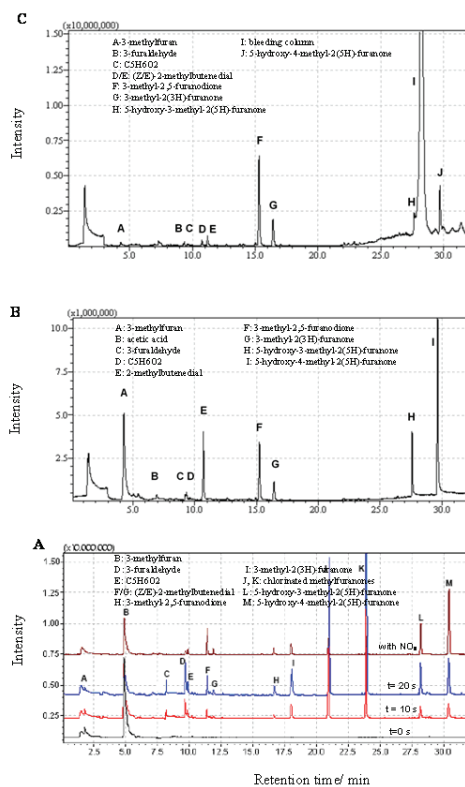


Fig. 3. Experimental chromatograms and the reaction products identified for the reactions of 3-methylfuran with chlorine atoms (A), hydroxyl radicals (B) and nitrate radicals (C) from SPME-GC/MS experiments.

22945

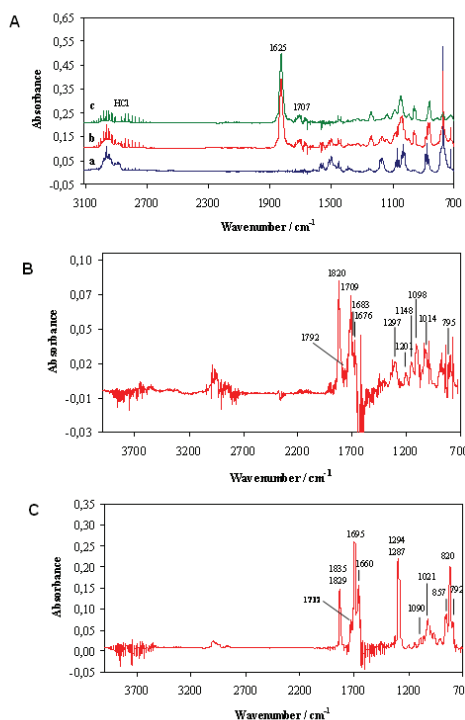
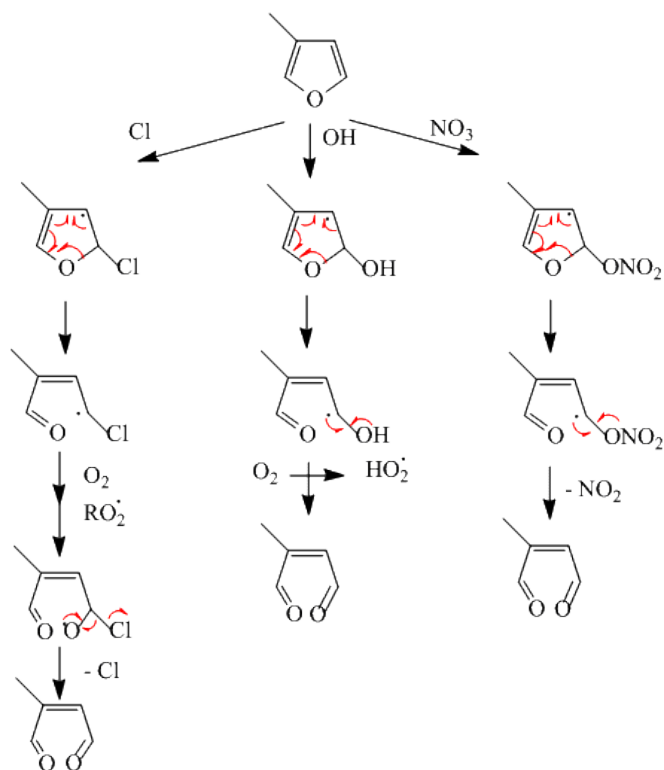


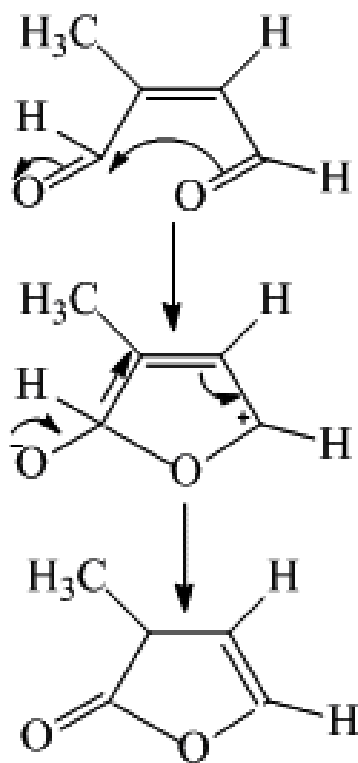
Fig. 4. Experimental infrared absorption spectra from the reaction of: (A) 3-methylfuran with chlorine atoms (a) before photolysis, (b) after 15 min of photolysis (c) residual spectrum from b after subtraction of 3-methylfuran, H₂O with the CO₂ absorption zeroed; (B) 3-methylfuran with hydroxyl radical (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).

22946



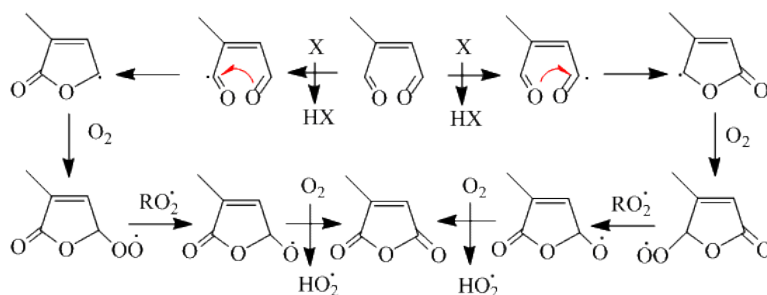
Scheme 1. Possible mechanisms for the formation of 2-methylbutenedial in the reaction of 3-methylfuran with Cl, OH and NO₃.

22947



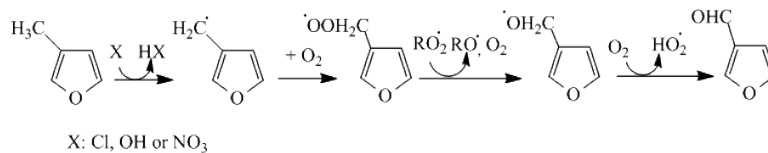
Scheme 2. Possible mechanism for the formation of 3-methyl-2(3H)-furanone from 2-methylbutenedial.

22948



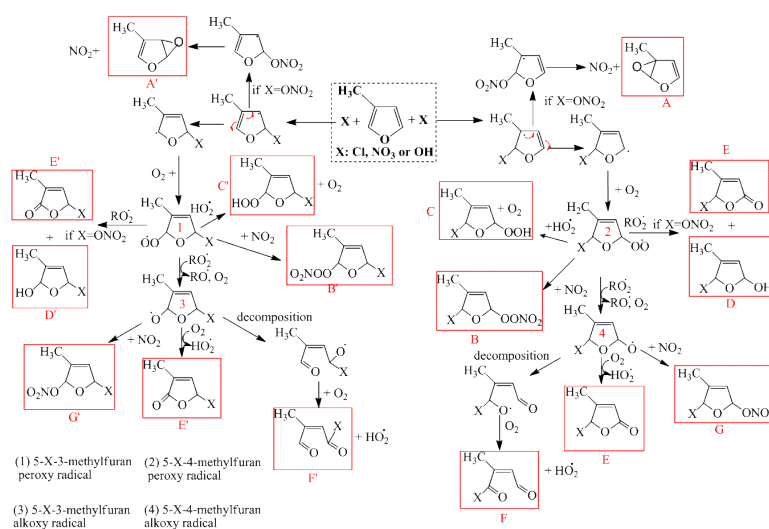
Scheme 3. Possible mechanisms for the formation of 3-methyl-2,5-furanodione in the reaction of 2-methylbutenodial with X, where X: Cl, OH or NO₃.

22949



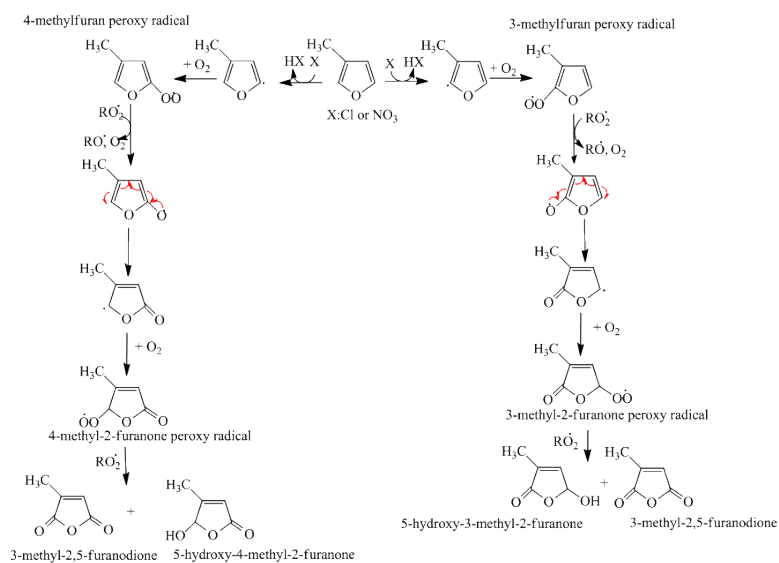
Scheme 4. Possible mechanisms for the formation of 3-furaldehyde in the reaction of 3-methylfuran with X, where X: Cl, OH or NO₃.

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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. Where X: Cl, OH or NO₃.

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

22952