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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 NO_3 radicals have been determined at room temperature and atmospheric pressure (air and N_2 as bath gases), using a relative method with different experimental techniques. The rate coefficients obtained for these reactions were (in units cm^3 $molecule^{-1}$ s^{-1}) $k_{OH} = (1.13 \pm 0.22) \times 10^{-10}$ and $k_{NO_3} = (1.26 \pm 0.18) \times 10^{-11}$. Products from the reaction of 3-methylfuran with OH, NO_3 and Cl atoms in the absence and in the presence of NO have also been determined. The main reaction products obtained were chlorinated methylfuranones and hydroxy-methylfuranones in the reaction of 3-methylfuran with Cl atoms, 2-methylbutenedial, 3-methyl-2,5-furanodione and hydroxy-methylfuranones in the reaction of 3-methylfuran with OH and NO_3 radicals and also nitrated compounds in the reaction with NO_3 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 NO_3 radicals. The formation of 3-furaldehyde and hydroxy-methylfuranones (in the reactions of 3-methylfuran with Cl atoms and NO_3 radicals) confirmed the H-atom abstraction from the methyl group and from the aromatic ring, respectively. This study represents the first product determination for Cl atoms and NO_3 radicals in reactions with 3-methylfuran. The reaction mechanisms and atmospheric implications of the reactions under consideration are also discussed.

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1 Introduction

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

The mixing ratios of 3-methylfuran were highly correlated with isoprene (Atkinson et al., 1984; Gu et al., 1995; Lee et al., 2005), which is the most abundant biogenic hydrocarbon emitted into the atmosphere with a global emission rate between 250 and 500 $Tg\,yr^{-1}$, exceeding that of anthropogenic hydrocarbons (Guenther et al., 2006; Laothawornkitkul et al., 2009). The reaction of isoprene with OH gives 3-methylfuran in an approximate yield of 3–7% depending presumably on the pressure (Ruppert and Becker, 2000; Lee et al., 2005). Therefore, and due to the high emission rates of isoprene, the potential atmospheric significance of the oxidation products (3-methylfuran) increases.

3-Methylfuran is expected to be very reactive with the main atmospheric oxidants. According to Atkinson et al. (1989), 3-methylfuran may play a role, albeit minor, in the chemical cycles in the lower troposphere. To date 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 obtained using a relative technique (Atkinson et al., 1989). Furthermore, two kinetic studies on the reaction of 3-methylfuran with the NO_3 radical have been published (Kind et al., 1996; Alvarado et al., 1996) and these gave two very different values for the rate

coefficient. In the case of the reaction with Cl atoms, the rate coefficient reported in the literature was obtained by Cabañas et al. (2005).

With regard to the reaction products, the data available in the literature are particularly scarce. A recent product study on the photooxidation of 3-methylfuran with HONO indicates that 2-methylbutenedial is the main gaseous product of the OH-oxidation of this compound (Gómez Álvarez et al., 2009). A theoretical computational study has also been published for this reaction and the conclusion was that direct hydrogen abstraction and nucleophilic bimolecular substitution play a minor or negligible role in the overall reaction (Zhang et al., 2008).
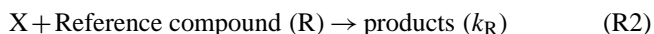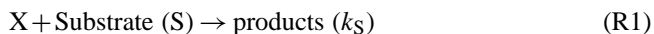
In the work described here the rate coefficients for the reaction of OH and NO_3 radicals with 3-methylfuran were determined in order to (i) assess the values previously reported in the literature as some discrepancies are apparent and (ii) to complete the kinetic study of alkylfurans initiated by our research group. Experiments were carried out at (298 ± 2) K and a total pressure of 1 atm using a relative rate method with LOOP/SPME-GC/FID/MS (Loop/Solid Phase Microextraction-Gas Chromatography/Flame Ionization Detection/Mass Spectrometry Detection) and FTIR (Fourier Transform Infrared Spectroscopy) as detection techniques for the organic compounds.

Products obtained in the reaction of 3-methylfuran with OH and NO_3 radicals and with Cl atoms were also characterised in order to propose degradation mechanisms for this compound in the atmosphere. This reaction product study was carried out using SPME-GC/FID/MS and FTIR as detection methods.

2 Experimental section

2.1 Kinetic study

Rate coefficients for the gas phase reactions of 3-methylfuran with the atmospheric oxidants, OH and NO_3 radicals, at (298 ± 2) K and ~ 1 atm of the total pressure in synthetic air and N_2, respectively, were determined using a relative rate method. The reactions of 3-methylfuran and reference compounds (with rate coefficients k_S and k_R, respectively) were monitored in the presence of OH or NO_3 radicals:

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

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

where X is OH or NO_3

As described in detail elsewhere (Atkinson et al., 1982) 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):

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

Thus, a plot of $\ln([S]_0/[S]_t)$ versus $\ln([R]_0/[R]_t)$ should be a straight line passing through the origin and the slope should give the ratio of rate coefficients k_S/k_R. Each reaction studied was measured relative to the reaction of different reference standards with oxidants X. In the case of 3-methylfuran with NO_3, a dilution term was included in Eq. (1) due to the special experimental procedure, which is described below. Therefore, for this reaction the equation required to obtain the rate coefficient is:

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

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 the reaction with OH or NO_3 radicals. In an effort to verify this assumption, various tests were performed to assess the loss of 3-methylfuran by reaction with precursors of OH and NO_3 radicals, photolysis and wall deposition. These processes, which could interfere with the kinetic determinations, were found to be negligible for 3-methylfuran and the selected reference compounds.

The experimental systems and the procedures used in this work are briefly described below. Further details can be found elsewhere (Cabañas et al., 2005; Villanueva et al., 2007, 2009). Only the FTIR system with a 50 L Pyrex glass vessel is described below in detail.

Three analytical systems were used in the experiments: 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 500 L bag for the experiments with NO_3 in order to minimize the dilution effect of the additions of N_2O_5. These bags were placed inside a rectangular cage with six VIS lamps ($\lambda_{max} = 360$ nm) mounted on the walls. The sampling methods included a system based on sample preconcentration, the solid phase microextraction technique (SPME) and a heated loop with a capacity of 1 cm^3 mounted in a six way valve. 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 capillary gas chromatography and detection by FID or MS. In all the experiments a capillary column (30 m × 0.3 mm id × 1.0 μm film thickness, Tracsil

TRB-1701, Teknokroma) was used to separate the compounds. The chromatographic conditions used for the analysis were as follows: injector 270 °C; detector 250 °C; temperature programme from 40 °C (4 min) to 120 °C (17 min) at a rate of 25 °C min^{-1}.

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

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

In the experiments performed with LOOP/GC-MS, benzene was used as the internal standard. The reactant mixtures were photolysed 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 about 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. Hydroxyl radicals were generated in the presence of NO by the photolysis of CH$_3$ONO (Atkinson et al., 1982) in air at a wavelength of 360 nm using the VIS lamps.

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

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

2.2 Products study

Product experiments were carried out at (298 ± 2) K with air at atmospheric pressure in different reaction chambers: (a) in a 150 L evacuable Teflon-coated chamber equipped with six 360 nm lamps and four 254 nm lamps and with the provision for sampling onto a 30/50 μm SPME (DVB/CAR/PDMS) fibre. The fibre adsorption and desorption time was 15 min at 270 °C in split/splitless mode for the GC injection port. The analysis in this case was carried out by GC/MS and GC/FID. Products were separated in the capillary column by applying the following temperature programme: from 40 °C (4 min) to 120 °C (12 min) at a rate of 25 °C min^{-1}, then at a rate of 10 °C min^{-1} up to 200 °C (10 min). Mass spectrometry detection was performed in electron 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 ($\lambda_{max} = 360$ nm) with in situ FTIR analysis for OH and NO$_3$ radicals; and (c) in a 1080 L quartz-glass reactor equipped with 10 low-pressure mercury lamps ($\lambda_{max} = 254$ nm) and 10 superactinic fluorescent lamps ($\lambda_{max} = 360$ nm) coupled with in situ FTIR analysis for Cl atoms. Details of this experimental set-up can be found elsewhere (Barnes et al., 1994).

In the quantitative analysis carried out by GC/FID, the response factor (RF) of each compound was determined by introducing different measured amounts of authentic standards (which covered the range of experimental conditions) into the Teflon chamber and conducting several replicate analyses with the coated SPME fibre. The response factor of each compound was calculated with the expression:

$$\text{Area} = \text{RF} \times [\text{product}] \tag{3}$$

where the area is quantified from the GC/FID chromatogram and the concentration of the product is known. For compounds that were not commercially available or the yield of the pure compound was not sufficient to carry out the calibration, only an estimation of yield was possible using the ECN (effective carbon number) method (Scalon and Willis, 1985).

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 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

Table 1. Rate coefficients for the reactions of 3-methylfuran with OH and NO$_3$ radicals at atmospheric pressure and room temperature.

Reaction	Reference	k_S/k_R^a	$k_{298\,K}^b/$ 10^{-10} cm^3 molec $^{-1}$ s^{-1}	$\bar{k}_{298\,K}/$ 10^{-10} cm^3 molec $^{-1}$ s^{-1}	Method	Bibliographic reference
3-Methylfuran + OH	*trans*-2-Butene	1.11±0.09	0.81±0.16		loop/GC-MS	This work
	5-Methylfurfural	2.27±0.08	1.16±0.06		SPME/GC-FID	This work
	trans-2-Butene	1.24±0.08	0.91±0.17	1.1±0.2^c	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$_3$	2-Methyl-2-butene	1.36±0.02	0.13±0.01		Loop/GC-FID	This work
	2-Methyl-2-butene	1.01±0.05	0.09±0.02	0.13±0.02^c	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)

^{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 $(7.31\pm1.31)\times10^{-11}$ cm^3 molec $^{-1}$ s^{-1} (Edney et al., 1986), $(5.10\pm0.20)\times10^{-11}$ cm^3 molec $^{-1}$ s^{-1} (Bierbach et al., 1995) and $(3.01\pm0.42)\times10^{-12}$ cm^3 molec $^{-1}$ s^{-1} (Nielsen et al., 1990), respectively; and a rate constant k_R for the reactions of NO$_3$ radicals with 2-methyl-2-butene and α-Pinene of $(9.38\pm3.32)\times10^{-12}$ cm^3 molec $^{-1}$ s^{-1} (Atkinson, 1991) and $(5.90\pm0.4)\times10^{-12}$ cm^3 molec $^{-1}$ s^{-1} (Martínez et al., 1998).

^{c} Weighted mean.

compound into the reactor or were taken from an existing IR spectral library bank.

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

2.2.1 Cl products

The experiments involving SPME GC/MS and GC/FID/ECD techniques were conducted in a Teflon bag ($\approx$150 L) placed inside a chamber with four 254 nm blacklamps. Photolysis of thionyl chloride (SOCl$_2$) or trichloroacetyl chloride (CCl$_3$COCl) was used to generate atomic chlorine in irradiation steps of 8 to 10 s for SOCl$_2$ and 10 to 60 s for CCl$_3$COCl. The total photolysis time was 30–90 s for SOCl$_2$ and 22–720 s for CCl$_3$COCl, with conversion of 3-methylfuran in the range 21–94%. 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 and only one qualitative experiment was carried out in the presence of NO. The initial concentrations of the reactants (in molecule cm^{-3} units) were as follows: [3-methylfuran] = (4.9–29) × 10^{13}, [CCl$_3$COCl] = (1.4–2.4) × 10^{14}, [SOCl$_2$] = (4.4–19) × 10^{13} and [NO] = 3.4 × 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 total photolysis time was in the range of 60–100 s in order to achieve 60–90% conversion of 3-methylfuran.

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

The initial concentrations of the reactants (in molecule cm^{-3} units) were as follows: [3-methylfuran] = (1.9–2.9) × 10^{13}, [Cl$_2$] = (4.9–7.3) × 10^{13} and [ClCOCOCl] = 1.2 × 10^{13}. 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 a resolution of 1 cm^{-1} 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. Two OH precursors were used in the GC/MS product studies in order to assess the influence of NO on the reaction mechanisms: H$_2$O$_2$ photolysed from 60 s to 60 min with the 254 nm lamps and CH$_3$ONO in the presence of NO photolysed from 20 to 30 s with the

360 nm lamps. After each photolysis a chromatogram was recorded and the total photolysis times of 150–180 s and 106 min for CH_3ONO and H_2O_2 were attained, respectively, to give 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: $[CH_3ONO] = (1.3–2.1) \times 10^{14}$, $[NO] = (3.2–4.4) \times 10^{13}$, $[3\text{-methylfuran}] = (3.6–12) \times 10^{13}$ and $[H_2O_2] = 2.8 \times 10^{14}$. In the quantitative analysis only CH_3ONO was used as the OH source.

In FTIR product experiments CH_3ONO was photolysed continuously with eight 360 nm lamps and this led to the conversion of up to 70% of the 3-methylfuran. 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 as follows: $[CH_3ONO] = 2.6 \times 10^{14}$, $[NO] = 2.6 \times 10^{14}$ and $[3\text{-methylfuran}] = 2.6 \times 10^{14}$.

2.2.3 NO$_3$ products

The products were identified by GC/FID/MS and FTIR spectroscopy. In the GC/FID/MS experiments the initial concentration of 3-methylfuran in the chamber (in molecule cm^{-3}) was 4.7×10^{13}. Successive additions of N_2O_5 were performed corresponding to a final concentration of 2.4×10^{13} molecule cm^{-3}, which resulted in the depletion of approximately 95% of the 3-methylfuran. In the FTIR experiments, the initial concentrations in the reactor (in molecule cm^{-3}) were as follows: $[N_2O_5] = (2.8–2.9) \times 10^{14}$ and $[3\text{-methylfuran}] = (2.4–2.9) \times 10^{14}$ to achieve 17% conversion of 3-methylfuran.

2.2.4 Chemicals

The chemicals 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-butenoic acid (Aldrich, 98%), $SOCl_2$ (Aldrich, +99%), CCl_3COCl (Aldrich, 99%) and $ClCOCOCl$ (Aldrich, 98%). Gaseous products: *trans*-2-butene (Aldrich, +99%), propene (Aldrich, +99%), 2-methyl-2-butene (Aldrich, +99%), Cl_2 (Praxair, >99.8%), N_2 (Praxair, 99.999%), air (Praxair, 99.999%) and NO (Praxair, 99%). The following compounds were used in methylnitrite synthesis: $NaNO_2$ (Panreac, 97%), H_2SO_4 (Panreac, 95–98%) and $CaCO_3$ (Riedel-de-Haën AG, 99%). In N_2O_5 synthesis: N_2O_4 (Fluka, >98.5%) and O_2 (Praxair, 99.999%). Hydroxymethyl-2(5H)-furanones [5-hydroxy-3-methyl-(5H)-furanone and 5-hydroxy-4-methyl-2(5H)-furanone] were prepared from 3-methylfuran according to Kumar and Pandey (2000). The product was characterised by GC-MS.
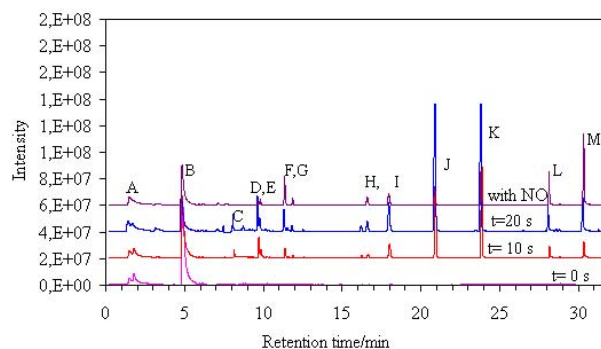

Fig. 1. Experimental chromatograms for the reactions of 3-methylfuran with chlorine atoms from SPME-GC/MS experiments.

3 Results and discussion

3.1 Kinetic studies

The data obtained for reactions of 3-methylfuran with OH and NO$_3$ radicals are plotted in accordance with Eqs. (1) and (2) (see Fig. 1 in the Supplement). The data give straight lines that pass through the origin with a slope of k_S/k_R, indicating that secondary reactions or heterogeneous processes are insignificant. The error limit for the ratio of rate coefficients k_S/k_R obtained from least-squares analyses includes only the precision of the fit to our experimental data ($\pm 2\sigma$). These rate constant ratios k_S/k_R are placed on an absolute basis using the recommended rate constants k_R for the reference compounds. The k_S error limit, σ_{kS}, was calculated taking into account the error limit from the slopes obtained from the regression analysis and the quoted error in the value of the rate coefficient for the reference compound. The weighted mean k_S values and the rate coefficient ratios k_S/k_R obtained by GC/FID and FTIR techniques are given in Table 1 together with the data available in literature.

The data show that within error there is no significant difference between runs monitored 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} cm^3 molecule^{-1} s^{-1}) show the high reactivity of OH radicals towards 3-methylfuran. The weighted mean rate coefficient data obtained for the reaction of 3-methylfuran with OH are slightly higher than the literature data (Atkinson et al., 1989) but these can be considered similar due to experimental errors. The rate coefficients for OH reactions can be estimated by the AOPWIM programme from the SAR method (Aschmann and Atkinson, 1995). The rate constant calculated in this way for 3-methylfuran and OH is 1.05×10^{-10} cm^3 molecule^{-1} s^{-1}, which is similar to the average rate coefficient value obtained in this work.

In relation to the reaction of 3-methylfuran with NO$_3$, the rate constant obtained in this work is consistent with the data obtained by Alvarado et al. (1996). A mean value between the rate constants for OH and NO$_3$ radicals determined in

this study and the ones obtained by Atkinson et al. (1989) and Alvarado et al. (1996) can, therefore, be proposed as a good reference value.

On the basis of the rate coefficients reported in Table 1 for the reaction of 3-methylfuran with OH and NO_3 radicals, together with data for Cl atoms reported in our previous work (Cabañas et al., 2005), the following order of reactivity can be established: $k_{Cl} > k_{OH} > k_{NO_3}$. A comparative study of these rate coefficients with values available in the literature for mono- and dimethylated furans was reported in a previous publication by Cabañas et al. (2005).

3.2 Product studies

The major challenge in identifying the reaction products from the reaction of 3-methylfuran with OH, NO_3 radicals and Cl atoms is the scarcity of commercially available standards. The identification of reaction products was carried out using the custom GC-MS and FTIR libraries created after the injection of commercial products, compounds synthesized in our laboratory, data from commercial GC-MS libraries (NIST 21, NIST 27, NIST 107, NIST 147 and WILEY 229) and Aldrich Library FTIR spectra (Pounchert, 1989).

3.2.1 Reaction with Cl atoms

An example of a typical GC-MS chromatogram is shown in Fig. 1 for the oxidation of 3-methylfuran by Cl atoms in the absence of NO at different reaction times and in the presence of NO (upper chromatogram). Peaks A and C represent artefact compounds from the chlorine source and from the fibre, respectively, and 3-methylfuran is represented by peak B. The compounds identified by the mass spectra and by the retention times of authentic standards are 3-furaldehyde (peak D), 3-methyl-2,5-furanodione (peak H) and 3-methyl-2(3*H*)-furanone (peak I). Analysis of the EI mass spectrum of peak E shows the presence of the compound $C_5H_6O_2$ and the chemical ionization (CI) mass spectrum of this peak shows that its molecular weight is 98. This peak can, therefore, be tentatively assigned to an isomer of 3-methyl-2(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 (see Fig. 2a and b). Peaks L and M are provisionally 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. The synthesis of the isomers of hydroxy-methylfuranones and the comparison with the commercial 5-hydroxy-4-methyl-2(5*H*)-furanone confirmed the identification of these compounds (see Fig. 2c and d). 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 com-
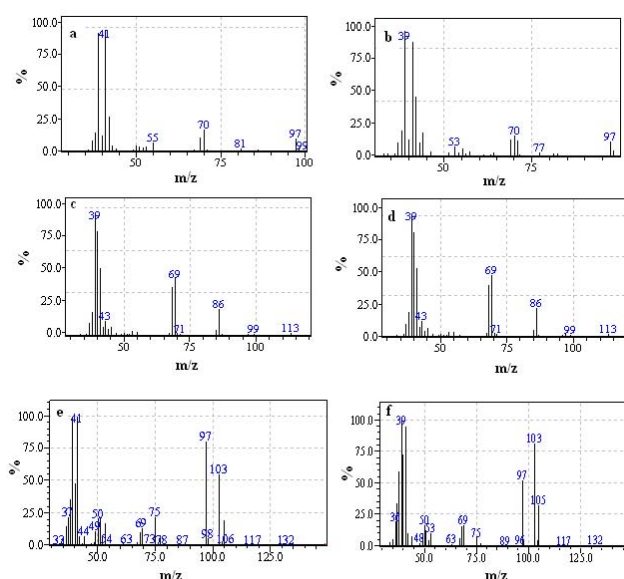

Fig. 2. **(a)** Experimental electron impact mass spectra (EI-MS) of peaks F (tr = 11.4 min) and G (tr = 11.8 min). **(b)** Experimental electron impact mass spectrum (EI-MS) of the 2-methylbutenedial synthesized. **(c)** Experimental electron impact mass spectrum (EI-MS) of peak L (tr = 28.2 min). **(d)** Experimental electron impact mass spectrum (EI-MS) of the commercial 5-hydroxy-4-methyl-2(5*H*)-furanone. **(e, f)** Mass spectra by electron impact ionization (EI) of peaks J and K assigned to a molecular formula $C_5H_5O_2Cl$.

pounds 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 (see Fig. 2 in the Supplement). The EI spectra of peaks J and K are shown in Fig. 2e and f. 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. It is, therefore, believed that peaks J and K can 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. 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. 1, the reaction products in the absence and in the presence of NO are similar. The only difference probably concerns the yields.
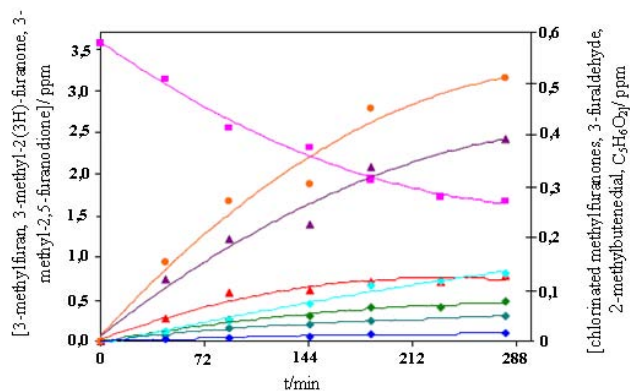
Fig. 3. Concentration-time profiles of 3-methylfuran and products identified in the reaction of 3-methylfuran with Cl atoms analysed by SPME-GC-FID: (■) 3-methylfuran, (◆) 3-furaldehyde, (◆) furanone isomer, $C_5H_6O_2$, (▲) 2-methylbutenedial, (◆) 3-methyl-2(3H)-furanone, (◆) 3-methyl-2,5-furanodione, (▲) chlorinated methylfuranone, (●) chlorinated methylfuranone.

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

An example of the concentration/time profiles for the identified products in the Cl atom initiated oxidation of 3-methylfuran is shown in Fig. 3. The curve contours for chlorinated methylfuranone, 3-furaldehyde and 2-methylbutenedial indicate that these are primary products. In the case of 3-furaldehyde, this fact is more evident in the plots obtained from FTIR analysis.

FTIR spectra recorded at different stages of the reaction of 3-methylfuran with Cl are shown in Fig. 4a: (a) spectrum of 3-methylfuran+Cl_2 in air before photolysis, (b) spectrum of 3-methylfuran and products after 15 min of photolysis (absorptions from CO_2 have been zeroed due to saturation of the band and those from H_2O have been subtracted), and (c) residual product spectrum after subtraction of 3-methylfuran. The residual spectrum of the products shows the presence of HCl and CO, a band with a high intensity at 1825 cm^{-1}, bands of medium intensity in the region 800–1300 cm^{-1} and two bands of low intensity in the carbonyl region at 1710 and 1665 cm^{-1}. Based on the results obtained by SPME-GC/MS the band at ~1710 cm^{-1} is assigned to 3-furaldehyde – an assignment also based on a comparison with the reference spectrum. The bands at ~1703 and 1665 cm^{-1} can be tentatively assigned to 2-methylbutenedial, but due to the low purity of the 2-methylbutenedial synthesized this can not be confirmed from the IR spectrum alone.

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
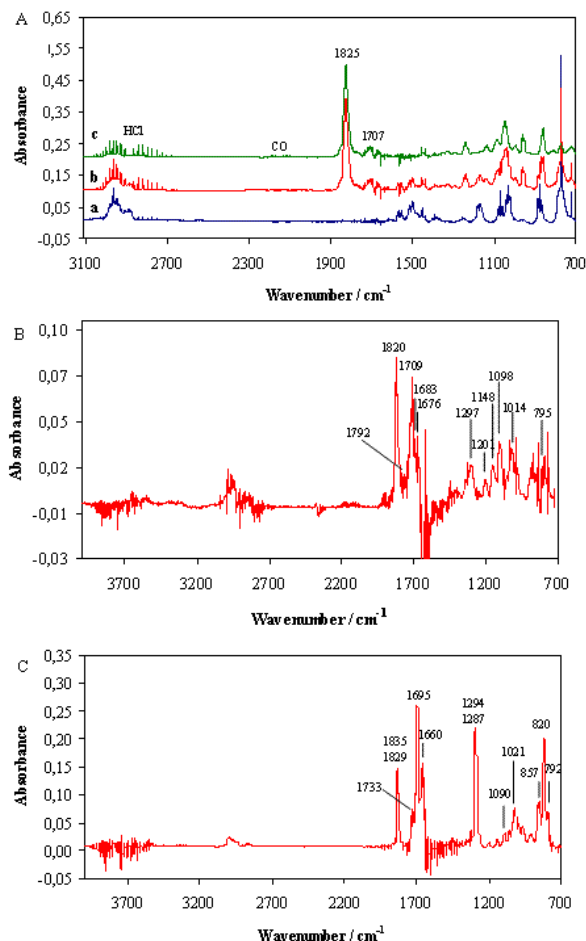

Fig. 4. Experimental infrared absorption spectra from the reaction of: **(A)** 3-methylfuran with chlorine atoms (a) before photolysis, (b) after 15 min of photolysis (c) residual spectrum from b after subtraction of 3-methylfuran, H_2O with the CO_2 absorption zeroed; **(B)** 3-methylfuran with hydroxyl 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).

(Villanueva et al., 2009), the band at 1825 cm^{-1} can be assigned to the chlorinated methylfuranone isomers 5-chloro-3-methyl-2(5H)-furanone and 5-chloro-4-methyl-2(5H)-furanone, because this band is very similar in appearance to that observed for 5-chloro-2(5H)-furanone. The possibility that this band could correspond to an acid chloride (3-methyl-4-oxo-2-butenoyl chloride or 2-methyl-4-oxo-2-butenoyl chloride) was ruled out as the infrared spectrum is devoid of any absorption bands in the region 2695–2900 cm^{-1}, which would be characteristic of the stretching vibration of C-H in the –CHO group.

The gas-phase IR absorption coefficients for chlorinated methylfuranones are not known. As a consequence, the concentrations of these compounds were estimated by applying the Beer–Lambert Law for the absorption band at 1825 cm^{-1} using the known absorption coefficient for the structurally

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

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	$C_5H_6O_2$	2 ± 1^a	–
16.7	112	3-methyl-2,5-furanodione		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	–
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.

related compound 2(5H)-furanone. The calculated yield of chlorinated methylfuranones is the sum of the concentrations of the two isomers as the IR spectrum is a mixture of the two individual ones. The yield of CO was not calculated because it is a secondary product that only appears at the end of the reaction.

The product yields were calculated from the slopes of plots of products formed versus 3-methylfuran reacted. 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 atoms was also considered using the rate coefficient obtained by Cabañas et al. (2008). A quantitative analysis in the presence of NO was not performed due to the occurrence of secondary reactions that involve the formation of OH in the reaction system (Wang et al., 2005). The molar yields obtained for the products identified by SPME/GC-FID and FTIR are given in Table 2 together with their retention times and molecular weights. The total error is a combination of statistical error 2σ obtained in a regression analysis and uncertainties estimated in the calibrations. Although it was not possible to quantify all of the identified compounds, if we compare the results from the quantification methods (SPME-

GC/FID and FTIR) it is clear that chlorinated methylfuranones are the major gas-phase reaction products in the reaction between Cl atoms and 3-methylfuran. Despite the overall uncertainties associated with each quantification method, the yields of the products are in fair quantitative agreement. A total carbon mass balance of 70% was obtained for the products detected in GC-FID experiments and 90% for the products determined by FTIR. These values must be treated with caution because the yield of chlorinated methylfuranones could be underestimated by GC-FID, as occurred in the case of the chlorinated furanone formed from furan and alkylfurans with Cl atoms, or overestimated in the case of FTIR (Villanueva et al., 2007, 2009).

3.2.2 Reaction with OH radicals

A typical GC-MS chromatogram of the reaction sample from the oxidation of 3-methylfuran by OH radicals in the presence of NO using CH_3ONO as a precursor for OH shows the same peaks as obtained in reaction of 3-methylfuran with Cl atoms – except for two peaks (see Fig. 3 in the Supplement). The compounds identified by the mass spectrum and by the retention time of authentic standards are acetic acid, 3-furaldehyde, 2-methylbutenedial, 3-methyl-2,5-furanodione,

3-methyl-2(3*H*)-furanone and 5-hydroxy-4-methyl-2(5*H*)-furanone. 5-Hydroxy-4-methyl-2(5*H*)-furanone was assigned by comparison with the mass spectrum and retention time of the commercial compound (see mass spectra c and d in Fig. 2). The presence of a compound of formula $C_5H_6O_2$ was evident, but this was not assigned to any particular structure. 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-butenoic acid by their mass spectra and retention times of authentic samples. Two peaks at 22.4 and 22.8 min were identified from the library as 4-methyl-2(5*H*)-furanone and methylsuccinic anhydride, but this is only a tentative identification because they were not compared with commercial standards. All of these new peaks can only be explained as being due to secondary reactions products, probably through photolysis ($\lambda = 254$ nm) of primary reaction products.

The yields in %C for 2-methylbutenedial, 3-furaldehyde, 3-methyl-2,5-furandione and 3-methyl-2(3*H*)-furanone were 1.4 ± 0.3, 3.9 ± 1.8, 18.1 ± 4.6 and 1.6 ± 0.2, respectively.

In order to complete or confirm the results obtained with SPME/GC-MS, different experiments using FTIR analysis were performed. However, the reaction products were only tentatively assigned due to the low signal intensity. The residual FTIR spectrum for the product obtained in the oxidation of 3-methylfuran with OH radicals in the presence of NO is shown in 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-furanodione was identified by comparison with the bands of an authentic standard (898, 1792 and 1858 cm^{-1}). The identification of 2-methylbutenedial by FTIR was not possible due to the low purity of the synthesized compound. Nevertheless, the absorption band at 1711 cm^{-1} (Fig. 4b) was assigned to 2-methylbutenedial by comparison with the bands of other 1,4-dicarbonyl compounds, such us Z-2-butenedial, and based on the results obtained by GC-MS. 2-Methylbutenedial was identified and quantified [yield of (83 ± 33)%] as a major reaction product by Gómez Álvarez et al. (2009) in the degradation of 3-methylfuran with OH radicals. The low yield (1.4%) obtained in our work could be due to secondary reactions that give products such as 3-methyl-2(3*H*)-furanone and 3-methyl-2,5-furanodione. In this way, Bierbach et al. (1995) reported that the yield of 4-oxo-2-pentenal (unsaturated 1,4-dicarbonyl compound) in the reaction of 2-methylfuran with OH radicals varied from ≈70% at the beginning of the reaction to ≈47% at the end due to photolysis of the compound and probably to the oxidation of the dicarbonyl compound by OH radicals (Bierbach et al., 1994; Tang and Zhu, 2005). In our experiments a significant decay in the intensity of the band at 1711 cm^{-1} with time was observed, meaning that a very fast loss process is occurring. The reason

why secondary reactions take place to a greater extent in our experiments than in those reported by Bierbach et al. (1995) and Gómez Álvarez et al. (2009) could concern the different experimental conditions used.

Absorption bands at 795, 1297 and 1734 cm^{-1} observed in the FTIR spectra are typical of nitroperoxy compounds ($ROONO_2$) formed from the reaction of peroxy radicals with NO_2 (Wängberg et al., 1997; Martín et al., 2002). One of the most intense bands was observed at 1820 cm^{-1} and this is assigned to a carbonyl group. This band, together with the bands observed at 1014, 1053, 1098 (typical of a C-O stretch of an alcohol group) and the band at 3500–3560 cm^{-1} (absorption characteristic of O-H), supports the formation of a hydroxy-methylfuranone as the reaction product. Based on the intensities of the peaks obtained by GC/MS, and taking into account that only 24% of the reacted carbon was identified, it is likely that different hydroxy-methylfuranones had been formed. However, hydroxy-methylfuranones were not quantified due to the low purity of the commercial compound. Compounds such as CO (2115 and 2176 cm^{-1}) and CO_2 (2360 cm^{-1}) were also evident and the intensity of their bands increased with time, which signifies that open compounds could be forming during the reaction.
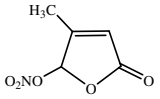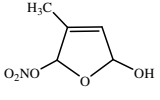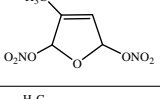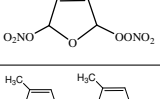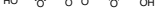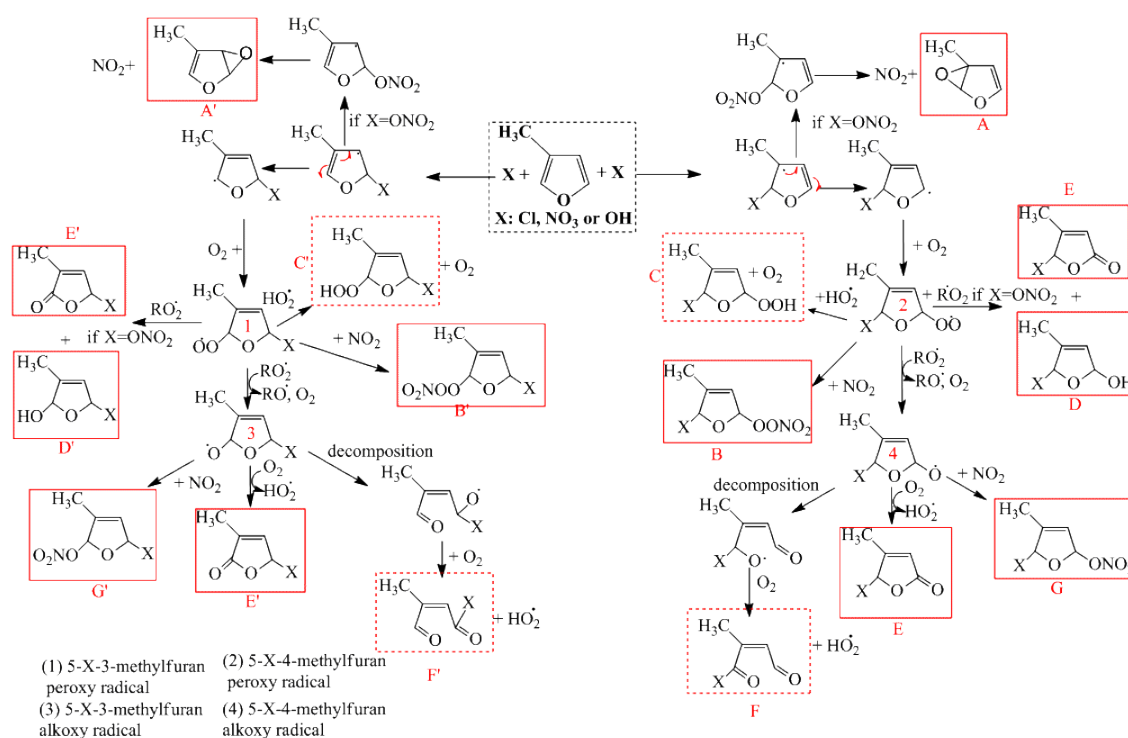
3.2.3 Reaction with NO_3 radicals

Analysis of GC-FID/MS chromatograms (see Fig. 3 in the Supplement) allowed the reaction products to be identified by their mass spectra and the retention times of authentic standards. The products were (Z/E)-2-methylbutenedial, 3-methyl-2,5-furanodione, 3-methyl-2(3*H*)-furanone and 5-hydroxy-4-methyl-2(5*H*)-furanone. These compounds have also been identified as reaction products in the reactions of 3-methylfuran with Cl and OH radicals. The yields in %C for the compounds identified were 0.45 ± 0.07 for 2-methylbutenedial, 0.36 ± 0.07 for 3-furaldehyde, 31.59 ± 2.51 for 3-methyl-2,5-furandione and 1.97 ± 0.25 for 3-methyl-2(3*H*)-furanone.

It is known from the literature that nitrated compounds should be present as products from the reaction of 3-methylfuran with NO_3 radicals. However, 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. As a result, different FTIR experiments were carried out in order to identify the nitrated compounds. 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. Due to the lack of nitrated standards, the absorption bands were assigned to different compounds based on the IR spectrum analysis and the general tropospheric degradation mechanisms (Finlayson-Pitts and Pitts, 2000; Villanueva et al., 2007).

The most important spectral features are listed in Table 3 together with their assignments. Absorption bands at 792,
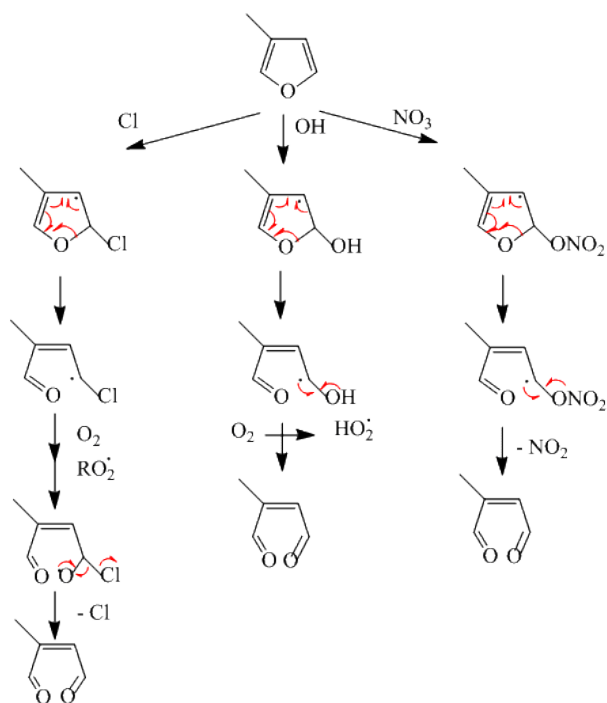
Table 3. Infrared spectral features and their tentative assignment to the products of the reaction of 3-methylfuran + NO$_3$.

	–ONO$_2$ (cm^{-1})	–OONO$_2$ (cm^{-1})	>CO (cm^{-1})	–CO (cm^{-1})	–OH (cm^{-1})
(structure)	857, 1287, 1660		1835–1829	1000–1100	
(structure)	857, 1287, 1695			1000–1100	3500–3650
(structure)	857, 1287, 1695			1000–1100	
(structure)	857, 1287, 1695	792,1294, 1732		1000–1100	
(structure)			1835–1829	1000–1100	3500–3650

Scheme 1. Reaction sequences of 3-methylfuran and X radical initiated by an addition process: possible mechanism for the formation of 5-X-3-methyl-2(5H)-furanone and 5-X-4-methyl-2(5H)-furanone. X: Cl, OH or NO$_3$. Compounds C/C$'$ and F/F$'$ were not detected.

1294 and 1732 cm^{-1} are attributable to nitroperoxy compounds (–OONO$_2$) based on the fact that nitroperoxy compounds decompose with time (Hjorth et al., 1990), a situation that was confirmed experimentally.

Absorption bands at 857, 1287, 1660 and 1695 cm^{-1} are attributable to nitroxy compounds (–ONO$_2$) considering that the typical bands of the –ONO$_2$ group appear at 843, 1296 and 1672 cm^{-1} (Tuazon et al., 1999). The presence of absorption bands at 1695 and 1660 cm^{-1} can be explained by

Scheme 2. Possible mechanisms for the formation of 2-methylbutenedial in the reaction of 3-methylfuran with Cl, OH and NO_3.

the shift of the absorption band at $1672\,\mathrm{cm^{-1}}$, with the magnitude of the shift depending on the functional group around the $-ONO_2$ group. Thus, the absorption band at $1695\,\mathrm{cm^{-1}}$ is attributed to a nitrooxy-hydroxyl compound and the band at $1660\,\mathrm{cm^{-1}}$ is attributed to a nitrooxy-carbonyl compound. The presence of absorption bands at 1000–$1100\,\mathrm{cm^{-1}}$, which could be due to a C-O stretch of an alcohol group or from the C-O stretch of a nitrate group, is evident in Fig. 4c. In the FTIR spectra the region 3000–$4000\,\mathrm{cm^{-1}}$ (O-H stretch) is characterised by a poor signal-to-noise ratio and it is, therefore, not possible to identify the compound(s) present. However, the general tropospheric degradation mechanism and different studies show that the formation of nitrooxy-hydroxyl and nitrooxy-carbonyl is possible.

Absorption bands at 1829–$1835\,\mathrm{cm^{-1}}$ are assigned to the carbonyl group of a lactone with an $-ONO_2$ group in the β-position. The effect of the $-ONO_2$ group on the carbonyl band in the lactone produces a similar displacement (to higher wavenumber) to that caused by Cl in chlorinated methylfuranones (Villanueva et al., 2007). Therefore, based on the results obtained with Cl and OH, the band at $1829\,\mathrm{cm^{-1}}$ together with the bands at 857, 1287, 1660 can be assigned to the isomers of nitrooxy-methyl-2(5H)-furanone.

The absorption band at $1021\,\mathrm{cm^{-1}}$ can also be assigned to a C-O stretch of an alcohol group of the hydroxyfuranone compounds (a compound that was positively identified by GC-MS analysis), where the negative conjugative

effect of the carbonyl group displaced the C-OH band to lower wavenumber. The absorption band at $820\,\mathrm{cm^{-1}}$ and the bands at $3000\,\mathrm{cm^{-1}}$ are assigned to a reaction product with an epoxy group (Pounchert, 1989). These absorptions decreased markedly with time, indicating that the possible epoxy compound formed in the reaction is thermally unstable. Epoxy compounds have been observed in others studies into the NO_3 radical (Wängberg et al., 1997; Martín et al., 2002). The simultaneous presence of these two sets of bands (792, 1294, 1732 and 857, 1287, 1660, 1695 $\mathrm{cm^{-1}}$) also suggests the formation of $R(ONO_2)(OONO_2)$-type compounds (Martín et al., 2002).

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

4   Reaction mechanism

According to the reaction products identified in this work and based on literature data, it can be concluded 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 (Cabañas et al., 2005; Gu et al., 1995; Jones and Ham, 2008; Martín et al., 2002; Picquet-Varrault et al., 2002; Rollins et al., 2009, Skov et al., 1992; Smith et al., 1999; Villanueva et al., 2007, 2009; Wang et al., 2005; Zhou et al., 2006). Therefore, in Schemes 1 and 2 reaction mechanisms for the reaction of 3-methylfuran and X radicals (OH, NO_3 or Cl) are proposed in order to account for the formation of the main reaction products identified in this study.

The sequence is initiated by the addition of radical X to the carbon-carbon double bond at the 2- and/or 5-positions. In the case of the NO_3 radical the resulting nitrooxyalkyl radicals can either decompose to form the epoxide (compounds A and/or A′) plus NO_2 (this process typically decreases in importance as the total pressure and O_2 content increases) or add O_2 to form nitrooxyalkyl peroxy radicals (5-ONO_2-3-methylfuran peroxyradical or 5-ONO_2-4-methylfuran peroxyradical) (Atkinson, 1991, 1997). The nitrooxyalkyl peroxy radicals can (a) react with NO_2 to form thermally unstable peroxydinitrates [$R(ONO_2)(OONO_2)$ compounds B and/or B′], (b) react with HO_2 radicals to form nitrooxy hydroperoxides (compounds C and/or C′) and (c) react with organic peroxy (RO_2) radicals. The reactions with organic peroxy radicals (including self-reaction) proceed (a) through a "molecular" channel, forming a nitrooxy alcohol and/or (if feasible) a nitrooxy carbonyl compound (compounds D and E and/or D′ and E′), and (b) through a "radical" channel to form the nitrooxy alkoxy radicals (5-ONO_2-3-methylfuran

alkoxyradical or 5-ONO$_2$-4-methylfuran alkoxyradical). The latter radicals are expected to (a) decompose to form dicarbonyl compounds as products (compounds F and/ or F′), (b) add NO$_2$ to form dinitrate compounds [R(ONO$_2$)(ONO$_2$) compounds G and/or G′] or (c) add molecular oxygen to form nitrooxycarbonyl compounds [compounds E and/or E′, 5-nitrooxy-2(5H)-methylfuranones] plus the HO$_2$ radical. Our FT-IR results are consistent with this scheme, with evidence for the formation of the epoxide (bands 820 cm^{-1} and 3000 cm^{-1} compound A or A′), nitrooxy alcohol (compound D or D′) and nitrooxy carbonyl (compounds E or E′). The same sequence of reactions could be initiated by OH and Cl radicals and the products formed would be the same on changing X (ONO$_2$) for Cl or OH. Compounds E and E′ would, therefore, be 5-chloro-2-(5H)-methylfuranones for the reaction of 3-methylfuran with Cl atoms and 5-hydroxy-2(5H)-methylfuranones for the reaction with OH radicals. However, in the reaction with Cl atoms and OH radicals there was no evidence in the product analysis for the formation of compounds D/D′, indicating that compounds E or E′ must be formed through a "radical" channel to yield alkoxy radicals.

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, NO$_3$, Cl), the process will be different (see Scheme 2). For the reaction with OH, the O$_2$ abstracts the H-atom whereas in the case of Cl atoms and the NO$_3$ radical the good characteristics of Cl and NO$_2$ as leaving groups mean that these groups are eliminated. This mechanism was also proposed by Bierbach et al. (1995) and Berndt et al. (1997).

The yield of 3-methyl-2(3H)-furanone can be explained by intramolecular photoisomerization of 2-methylbutenedial in the presence of VIS and UV radiation (Scheme 1, Supplement) (Bierbach et al., 1994). In the case where X is NO$_3$ there is no radiation but the presence of HNO$_3$ probably stabilizes the zwitterionic intermediate and, thus, favours the process. 3-Methyl-2,5-furanodione can be formed by abstraction of the aldehydic hydrogen of 2-methylbutenedial with the radical X (Bierbach et al., 1994) (see Scheme 2 in the Supplement). In this case, 3-methyl-2,5-furanodione would be a secondary product and the yield of this, together with the yield of 3-methyl-2(3H)-furanone, would give 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.

The presence of 3-furaldehyde as a primary product can be explained by the attack of the radical X to 3-methylfuran with abstraction of an H-atom from the methyl group to form a furfuryl radical, which evolves to form 3-furaldehyde (Scheme 3 in the Supplement). However, based on the yield obtained in this study (where the highest yield is about 7% for the Cl reaction) this process is not as favoured as the addition route.

Table 4. Atmospheric lifetimes for 3-methylfuran.

Oxidant	$k/10^{-10}$ cm^3 molecule^{-1} s^{-1}	τ
OH	1.13	2.5 h[a]
NO$_3$	0.12	1 h[b]
Cl	4.2	3 days[c,d]
O$_3$	2.05×10^{-7}	1 day[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 [NO$_3$] = 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 a kinetic rate coefficient for the reaction with O$_3$ molecules at 298 K (Alvarado et al., 1996) and on the basis of the average concentrations in the troposphere of [O$_3$] = 7.4×10^{11} molecule cm^{-3} (Logan, 1985).

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

In conclusion, the addition process with retention of configuration is the most important pathway for the reaction of 3-methylfuran with Cl atoms. This fact is corroborated by the high yields of 5-chloro-2(5H)-methylfuranones. In the case of the reaction with OH the dominant reaction pathway is ring opening, although it is believed that 5-hydroxy-2(5H)-methylfuranone (product with retention of configuration) is

a significant product, although it could not be quantified. For the reaction with NO_3, 5-nitrooxy-2($5H$)-methylfuranones (products with retention of configuration) were not identified by GC/MS and they were only tentatively assigned to certain bands in the IR spectrum. The formation of these compounds is probably consistent with the results obtained in the OH and Cl reactions. In addition, due to the low yield obtained for 2-methylbutenedial it is not possible to determine the dominant reaction pathway.

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. Indeed, this process will yield the same products as obtained from furan, but with the corresponding methyl group (Villanueva et al., 2007).

5 Atmospheric implications

The kinetic data obtained in this study can be used to calculate atmospheric lifetimes for 3-methylfuran due to reaction with the oxidants OH, NO_3, Cl and O_3 by applying Eq. (4)

$$\tau_{total} = \frac{1}{k_X[X]} \tag{4}$$

The average (24 h) concentrations of these compounds in the troposphere are as follows: $[OH] = 1 \times 10^6$ radicals cm^{-3} (Prinn et al., 1992), $[NO_3] = 2 \times 10^7$ radicals cm^{-3} (Finlayson-Pitts and Pitts, 2000), $[O_3] = 7.4 \times 10^{11}$ molecule cm^{-3} (Logan, 1985), and $[Cl] = 1 \times 10^4$ atoms cm^{-3} (Wingenter et al., 1996) assuming an average concentration of chlorine atoms in the global marine boundary layer. As shown in Table 4, OH and NO_3 radicals are globally the most important sinks for 3-methylfuran at daytime and nighttime, respectively, with lifetime values of 2.5 and 1 h, but chlorine will compete with these oxidants as a sink in coastal urban areas where its concentration increases at dawn (Spicer et al., 1998). The lifetimes given in Table 4 provide only an approximate estimate of the global mean lifetime because the use of average radical concentrations is really not appropriate for such a short lived species.

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 publication (Villanueva et al., 2009), certain chlorinated compounds, such as the chlorinated-methylfuranones determined in this work, are formed in the atmosphere by the reaction of Cl atoms with the parent VOC. Therefore, if a chlorinated product can be identified from a particular reaction involving Cl, these products could serve as "markers" in the chemistry of Cl atoms in the troposphere.

On the other hand, the majority of compounds identified from the reaction of 3-methylfuran with NO_3 are nitrated compounds. These compounds can act as NO_x reservoir species (or sinks), especially during the night.

In recent years, the California Air Resources Board (CARB) has adopted regulations for volatile organic compounds (VOCs) based on calculations of their relative ground-level ozone impacts. For the purposes of these regulations, the impact levels are quantified using the Maximum Incremental Reactivity (MIR) scale. This scale was developed by Carter (1994) 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_{O_3}/g_{VOC} (Carter, 2010). This value indicates 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.net/11/3227/2011/ acp-11-3227-2011-supplement.zip.

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