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Gas-phase degradation of 2-butanethiol initiated by OH radicals and Cl atoms: kinetics, product yields and mechanism at 298 K and atmospheric pressure†

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Relative rate coefficients and product distribution of the reaction of 2-butanethiol (2butSH) with OH radicals and Cl atoms were obtained at atmospheric pressure and 298 K. The experiments were performed in a 480 L borosilicate glass photoreactor in synthetic air coupled to a long path "*in situ*" FTIR spectrometer. The rate coefficients obtained by averaging the values from different experiments were: $k_{OH} = (2.58 \pm 0.21) \times 10^{-11}$ cm^3 per molecule per s and $k_{Cl} = (2.49 \pm 0.19) \times 10^{-10}$ cm^3 per molecule per s. The kinetic values were compared with related alkyl thiols and homologous alkyl alcohols, where it was found that thiols react faster with both oxidants, OH radicals and Cl atoms. SO$_2$ and 2-butanone were the major products identified for the reactions of 2-butanethiol with OH radicals and Cl atoms. The product yield of the reaction of 2-butanethiol and OH radicals were $(81 \pm 2)\%$, and $(42 \pm 1)\%$ for SO$_2$ and 2-butanone, respectively. For the reactions of 2-butanethiol with Cl atom, yields of SO$_2$ and 2-butanone were $(59 \pm 2)\%$ and $(39 \pm 2)\%$, respectively. A degradation mechanism was proposed for the pathways that leads to formation of identified products. The product distribution observed indicated that the H-atom of the S−H group abstraction channel is the main pathway for the reaction of OH radicals and Cl atoms with 2-butanethiol.

1 Introduction

In the atmosphere, sulfur is central to many environmental issues including acid rain and climate change. Volatile Organic Sulfur Compounds (VOSCs) can exist at high concentrations and they are released into the environment from natural emissions and anthropogenic sources.[1–5] Human activity is closely related to the increase of pollution in different environmental settings, VOSCs could contribute 35–40% of VOCs emitted during the aerobic composting processes of food wastes[1] due to high contents of organic matter and moisture. Other anthropogenic sources of VOSCs include landfill facilities[3] heavy polluted rivers and creeks.[5,6] All these sources contribute to the rising concentrations of VOCS in the air of cities with high population density.[7]

The main and most studied VOSCs are H$_2$S, CS$_2$ and dimethyl sulfide (DMS).[8–13] However, in recent years, alkyl thiols

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have aroused great interest, especially because of the experimental evidence about their presence in various environmental systems.[3,4,14] 2-Butanethiol was detected in samples of air from sewerage treatment tanks of chemical petroleum, geothermal areas, muddy beach water and wastewater treatment plants.[2,15–18]

There are several experimental and theoretical studies of the reactions of alkyl thiols with Cl atoms and OH radicals.[19–27] In all cases the rates coefficients for Cl-atoms were an order of magnitude faster than the corresponding reaction with OH radical. Hence, tropospheric concentrations of Cl need to be atmospherically important to their reactions compete with OH radicals. Cl-atoms concentrations could be significant at the marine boundary layer[28] and even in the mid-continental areas due to the presence of ClNO$_2$ precursor at significant levels, as reported in field measurement observations on regions remote from the coastline.[29]

The dominant fate of VOSCs in the atmosphere is the chemical transformations to produce sulfur dioxide and carbonyl compounds, where these gas species can contribute to acid rain as well as aerosol and cloud formation, affecting the climate and the radiation balance.[3,30,31] Some authors discussed the role of the VOSC in atmospheric chemistry as primary irritant and ubiquitous offensive odor pollutants with very low

sensory thresholds.[3,4,6] Friedman *et al.*[32] proposed that even a small anthropogenic perturbation of SO_2 concentrations could impact the oxidation chemistry of biogenic VOCS, increasing the aerosol acidity and ammonium sulphate aerosol formation. Additionally, exposure to high levels of sulfur dioxide in the air can cause breathing difficulties, obstructing airways, bronchitis and other respiratory illness.[33] A knowledge of kinetics and mechanisms of the oxidation of these sulphur containing compounds is relevant to understand their chemistry and impact in the atmosphere.

In this work, we investigate the kinetics, mechanism and products yields of the reactions of 2-butanethiol with Cl atoms and OH radicals. There are two previous studies of the kinetics of the reaction of 2-butanethiol with Cl atoms at low pressure (0.75 Torr) and at atmospheric pressure.[26,27] This work represents the first study of identification and quantification of reaction products. As far as we know there is not previous work for reaction of 2-butanethiol with Cl atoms at atmospheric conditions of pressure and temperature. Atmospheric implications of the reactions studied are discussed.

2 Materials and methods

2.1 Experimental procedures

Both kinetic determinations and products distributions experiments were performed at atmospheric pressure of synthetic air and 298 ± 2 K in an atmospheric simulation chamber. Detailed description of the reactor used can be found elsewhere.[34] A brief description of the system is given here. The chamber is composed of a cylindrical borosilicate glass vessel (3 m in length and 45 cm inner diameter) closed at both ends by aluminium end flanges with a total volume of 480 L. The reactor contains 32 fluorescent lamps (Philips TLA 40 W, $300 \leq \lambda \leq 450$ nm, $\lambda_{max} = 360$ nm) spaced evenly around the outside of the reactor. To ensure homogeneous mixing of the reactants, a magnetically coupled Teflon mixing fan was placed inside the chamber. The system is evacuated by a pumping system consisting of a turbo-molecular pump backed by a double stage rotary fore pump to 10^{-3} Torr. The detection system is a FTIR spectrometer Nicolet Magna 520 equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT). The beam is reflected into the chamber and a White-type mirror system mounted internally in the chamber enables *in situ* monitoring of the reactants in the infrared range 4000–700 cm^{-1}. The White mirror system was operated with the total optical absorption path length set to 48.11 m and infrared spectra were recorded with a spectral resolution of 1 cm^{-1}. Typically, 64 interferograms were co-added per spectrum over a period of approximately 1 minute and 15 spectra were recorded per experiment.

The initial concentration employed of reactants in ppmV (1 ppmV = 2.46×10^{13} molecule per cm^3 at 298 K) were: (9.0–9.5) ppmV for 2butSH; (9.0–9.5) ppmV for 2-methyl-propene; (8.0–9.0) ppmV for propene; (9.0–9.5) ppmV for *E*-2-butene; (20.0–20.5) ppmV for methyl nitrite and (10.0–10.5) ppmV for chlorine.
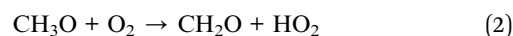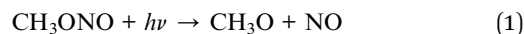
The following chemicals, with purities as stated by the supplier, were used without further purification: synthetic air

(Air Liquide, 99.999%), 2-butanethiol (Merk 99%), isobutene (Messer Griesheim, 99%), *E*-2-butene (Messer Griesheim, 99%), and Cl_2 (Messer Griesheim, >99.8%).

Methyl nitrite was prepared by the drop-wise addition of 50% sulphuric acid to a saturated solution of sodium nitrite in water and methanol. The reactions products were carried through a concentrated solution of sodium hydroxide and over anhydrous calcium chloride into a trap cooled at dry-ice temperature.[35] Methyl nitrite was collected and stored at 193 K purity was confirmed by IR spectroscopy.

2.2 Kinetic and product distribution analyses

OH radicals were generated by the photolysis of CH_3ONO/air mixtures with the fluorescent lamps,

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \tag{1}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{2}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{3}$$

and chlorine atoms were generated by the photolysis of Cl_2 in air, also with the fluorescent lamps:

$$Cl_2 + h\nu \rightarrow 2Cl \tag{4}$$

Once formed the oxidant species X (OH radicals or Cl atoms), it reacts with both the 2-butanethiol (2butSH) and reference compounds (R) in the following way:

$$X + 2butSH \rightarrow products \tag{5}$$

$$X + R \rightarrow products \tag{6}$$
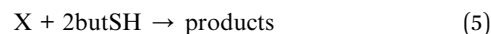
The relative rate technique was used to obtain the rate coefficients of the title reactions. In steady-state concentrations conditions of the oxidants species, the relative rate technique is based in the assumption that both 2butSH and reference compound are consumed only by reactions (5) and (6) and the reactions are competitive with each other. A graphical relationship between the first order decays of reactants and the rate coefficients of reactions (5) and (6) can be obtained in the following way:

$$\ln\left(\frac{[2butSH]_0}{[2butSH]_t}\right) = \frac{k_5}{k_6}\ln\left(\frac{[R]_0}{[R]_t}\right) \tag{7}$$

Plots of $\ln([2butSH]_0/[2butSH]_t)$ *versus* $\ln([R]_0/[R]_t)$ should yield straight lines with slope k_5/k_6, where $[2butSH]_0$, $[R]_0$, $[2butSH]_t$ and $[R]_t$ are the concentrations of 2butSH and reference compounds before irradiation and at time t, respectively, and k_5 and k_6 are the rate coefficients of reactions (5) and (6) respectively.

In order to test the presence of secondary reactions various tests were performed: (i) mixtures of reactants with synthetic air in absence of radical precursor species, were irradiated for 30 minutes using the fluorescent lamps checking possible photolysis of the reactants. (ii) Mixtures of reactants with
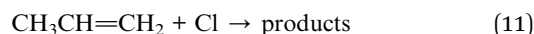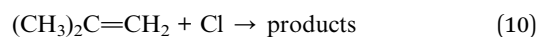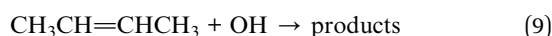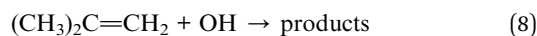
synthetic air in absence of radical precursor species were prepared in order to test deposition or wall losses of reactants and (iii) mixtures of reactants with chlorine or methyl nitrite were prepared and allowed in the dark for 30 minutes to test for reaction of the reactants with the radical precursor before irradiation. Photolysis, wall losses and dark reactions of reactants with oxidant precursor were negligible over the typical periods of time employed in this study.

For reaction products studies, mixtures of 2butSH and chlorine or methyl nitrite in synthetic air were irradiated using fluorescent lamps. 5 spectra was taken before irradiation to test initial conditions. Then, 10 more spectra were taken with the lamps on to generate reaction products. The reference spectrum of reactants were subtracted to each reaction spectrum. Then, residual spectrum was compared with calibrated reference spectra stored in the IR spectral database at the University of Wuppertal.

3 Results and discussion

3.1 Relative rate coefficients with OH radicals and Cl atoms

The rate coefficients for the reactions of 2butSH with OH radicals and Cl atoms were experimentally obtained at (298 ± 2) K and atmospheric pressure of synthetic air. The rate coefficients for the title reactions were obtained relative to the rate coefficients of 2-methyl-propene and E-2-butene for the OH radicals, and 2-methyl-propene and propene for Cl atoms according with the following reactions:

$$(CH_3)_2C{=}CH_2 + OH \rightarrow products \tag{8}$$

$$CH_3CH{=}CHCH_3 + OH \rightarrow products \tag{9}$$

$$(CH_3)_2C{=}CH_2 + Cl \rightarrow products \tag{10}$$

$$CH_3CH{=}CH_2 + Cl \rightarrow products \tag{11}$$

where k_8 $(5.14 \pm 1.03) \times 10^{-11}$,[36] k_9 $(6.39 \pm 1.28) \times 10^{-11}$,[37] k_{10} $(3.40 \pm 0.28) \times 10^{-10}$ (ref. 38) and k_{11} $(2.64 \pm 0.21) \times 10^{-11}$ (ref. 38). All values are expressed in cm³ per molecule per s.

The data were fitted to a straight line by linear least-squares procedure and the rate coefficients was obtained from eqn (7). Plots of kinetic data for the reactions of OH and Cl with 2butSH with different references are shown in Fig. 1 and 2. A minimum of three experiments were made with each reference, however, only one example is show for clarity. A good agreement was obtained between the results of experiments with different references (Table 1). The rate coefficients, obtained by averaging the values from different experiments, are the following:

$$k_{OH} = (2.58 \pm 0.55) \times 10^{-11} \text{ cm}^3 \text{ per molecule per s}$$

$$k_{Cl} = (2.49 \pm 0.70) \times 10^{-10} \text{ cm}^3 \text{ per molecule per s}$$

The uncertainties are a combination of the 2 s statistical errors from the linear regression analysis and a contribution to cover errors in the rate coefficients of the reference compounds.
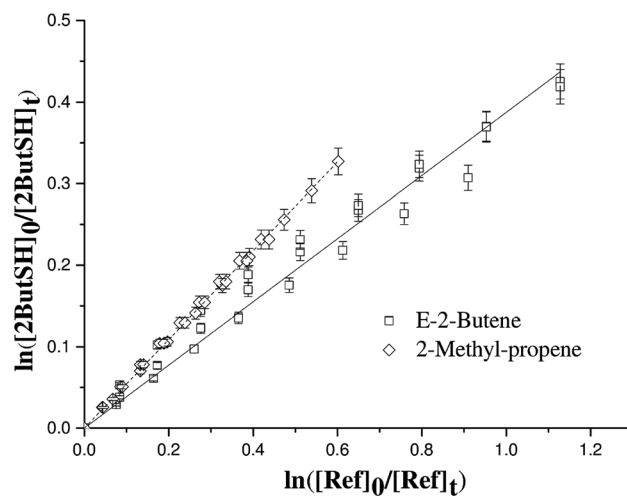

Fig. 1 Plots of kinetic data of reaction of 2butSH with OH radicals at 298 K and atmospheric pressure of synthetic air using 2-methyl-propene and E-2-butene as reference compounds.

We can notice that the value of k_{Cl} is almost an order of magnitude larger than the value for k_{OH}. This may mean, that the atmospheric degradation with chlorine atoms could be important, if Cl atoms concentrations are significant. The reported values for k_{OH} are bigger than the obtained in this study $(\sim 3.8 \times 10^{-11}$ cm³ per molecule per s).[26,27] We think that this could be related with the differences in the experimental conditions. The absolute value of Wine et al.[27] was obtained at low pressure conditions (75 Torr). While, the relative value of Barnes et al.[26] was obtained at higher concentrations of reactants that those used in this study (Table 1).

On the other hand, the value k_{Cl} determined in this study is the first reported rate coefficient for the reaction of Cl atoms with 2butSH, and therefore no direct comparison with literature can be made. However, a comparison of the rate coefficients
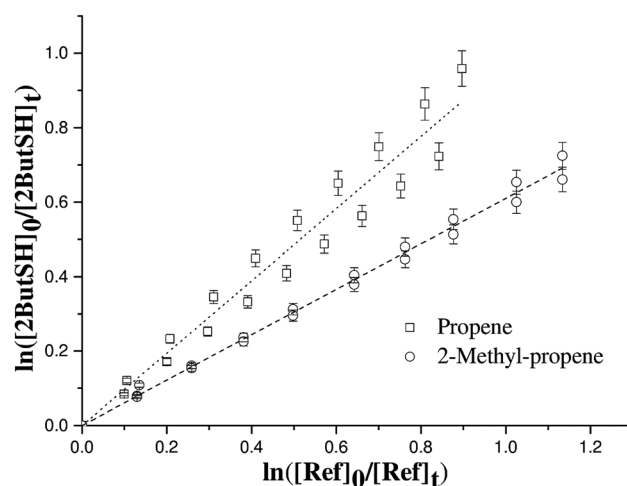

Fig. 2 Plots of kinetic data of reaction of 2butSH with Cl atoms at 298 K and atmospheric pressure of synthetic air using 2-methyl-propene and propene as reference compounds.

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Table 1 Slopes $k_{2butSH}/k_{reference}$ and rate coefficients obtained for the reactions of 2butSH with OH radicals and Cl atoms at (298 ± 2) K and atmospheric pressure of synthetic air

Reaction	Reference	$k_{2butSH}/k_{reference}$	$k_{2butSH}{}^a$
$CH_3CH_2CH(SH)CH_3$ + OH	$(CH_3)_2C{=}CH_2$	0.540 ± 0.001	$(2.78 \pm 0.28) \times 10^{-11}$
	$(CH_3)_2C{=}CH_2$	0.537 ± 0.003	$(2.76 \pm 0.29) \times 10^{-11}$
	$(CH_3)_2C{=}CH_2$	0.563 ± 0.003	$(2.89 \pm 0.30) \times 10^{-11}$
	$CH_3CH{=}CHCH_3$	0.341 ± 0.005	$(2.19 \pm 0.08) \times 10^{-11}$
	$CH_3CH{=}CHCH_3$	0.396 ± 0.006	$(2.53 \pm 0.10) \times 10^{-11}$
	$CH_3CH{=}CHCH_3$	0.402 ± 0.013	$(2.57 \pm 0.14) \times 10^{-11}$
	$CH_3CH{=}CHCH_3$	0.369 ± 0.011	$(2.36 \pm 0.12) \times 10^{-11}$
	Average		***(2.58 ± 0.55) × 10⁻¹¹***
$CH_3CH_2CH(SH)CH_3$ + Cl	$(CH_3)_2C{=}CH_2$	0.634 ± 0.002	$(2.14 \pm 0.18) \times 10^{-10}$
	$(CH_3)_2C{=}CH_2$	0.764 ± 0.002	$(2.58 \pm 0.22) \times 10^{-10}$
	$(CH_3)_2C{=}CH_2$	0.686 ± 0.001	$(2.32 \pm 0.20) \times 10^{-10}$
	$CH_3CH{=}CH_2$	1.075 ± 0.002	$(2.84 \pm 0.24) \times 10^{-10}$
	$CH_3CH{=}CH_2$	0.990 ± 0.002	$(2.61 \pm 0.21) \times 10^{-10}$
	$CH_3CH{=}CH_2$	0.924 ± 0.001	$(2.44 \pm 0.20) \times 10^{-10}$
	Average		***(2.49 ± 0.70) × 10⁻¹⁰***

[a] cm³ per molecule per s.

determined in this study with the literature values of another alkyl thiols and homologous alcohols is shown in (Table 2). In almost all cases the reactions of OH radicals and Cl atoms with alkyl thiols are faster than with the homologous alcohols. A possible reason for this behaviour could be that the H-abstraction in the reactions with OH radicals and the corresponding reactions with Cl atoms with alkyl alcohols appears to occur exclusively from the C–H bonds.[39] Meanwhile, the very stable prereactive complex formed during the reaction with alkyl thiols, where in both cases the sulfur seems to be bound to the reactive species (OH or Cl) favour the H-abstraction on the S–H group which is more favoured thermodynamically.[24,40] In these sense, the value reported for $CH_3CH_2CH_2CH_2SH$, lower than its homologous alcohol, was obtained at reduced pressure,[24] which could avoid the formation of the prereactive complex, affecting the value of the rate coefficient.

We cannot conclude that there is a relationship between the rate coefficient with the length of the carbon chain, despite observing a slight increase in the value of the rate coefficient by increasing the number of alkyl groups in reactions with the OH radicals. In the reaction with Cl atoms, the values are very close to the collision limit, as to propose a relationship with the length of the alkyl chain. This fact is in agreement with previous

reports that indicate the lack of selective nature of Cl atoms reactions, it seems that the reactivity of chlorine atoms against the VOCS is less affected with any long range effect or interaction in gas phase reactions.[39,41]

3.2 Reaction products study

Further experiments were made to investigate the mechanism and the product distribution of OH radicals and Cl atoms initiated oxidation of 2-butanethiol under similar conditions of the kinetic experiments.

3.2.1 2-Butanethiol + OH oxidation. Fig. 3 shows the usual IR spectra obtained during the reaction. Trace A shows the IR spectrum for a mixture of 2butSH and methyl nitrate (CH_3ONO) in air acquired before irradiation and trace B shows the spectrum after irradiation and subtraction of the 2butSH and CH_3ONO absorptions. Traces C, D, E, F and G show the reference spectra for SO_2, 2-butanone, formaldehyde (HCHO), formic acid (HC(O)OH) and peroxyacetyl nitrate (PAN), respectively, which have been identified as reaction products of 2-butSH with OH radicals. Finally, the trace H shows the residual spectrum after to subtract the spectra of the identified products. SO_2, 2-butanone and HCHO are the main primary products identified. PAN and HC(O)OH are formed from

Table 2 Rate coefficients of alkyl thiols and alkyl alcohols with OH radicals and Cl atoms at 298 K of temperature

Alkyl group	k_{OH} $(\times 10^{-11})^a$		k_{cl} $(\times 10^{-10})^a$	
	R = OH	R = SH	R = OH	R = SH
CH_3R	0.10 ± 0.02^b	3.60 ± 0.40^d	0.56 ± 0.06^e	2.0 ± 0.34^g
CH_3CH_2R	0.35 ± 0.05^b	4.50 ± 0.50^d	1.01 ± 0.06^b	1.9 ± 0.20^h
$CH_3CH_2CH_2R$	0.55 ± 0.04^b	5.30 ± 0.60^d	1.49 ± 0.07^b	2.37 ± 0.66^i
$(CH_3)_2CH_2R$	0.58 ± 0.08^b	3.90 ± 0.40^d	0.84 ± 0.04^b	2.70 ± 0.60^h
$CH_3CH_2CH_2CH_2R$	0.86 ± 0.07^b	5.60 ± 0.40^d	2.04 ± 0.14^b	1.58 ± 0.40^j
$CH_3CH_2CH(R)CH_3$	0.88 ± 0.15^c	2.58 ± 0.55^k	1.32 ± 0.14^f	2.49 ± 0.70^k

[a] cm³ per molecule per s. [b] Ref. 39. [c] Ref. 43. [d] Ref. 26. [e] Ref. 53. [f] Ref. 54. [g] Ref. 55. [h] Ref. 20. [i] Ref. 56. [j] Ref. 54. [k] This work.
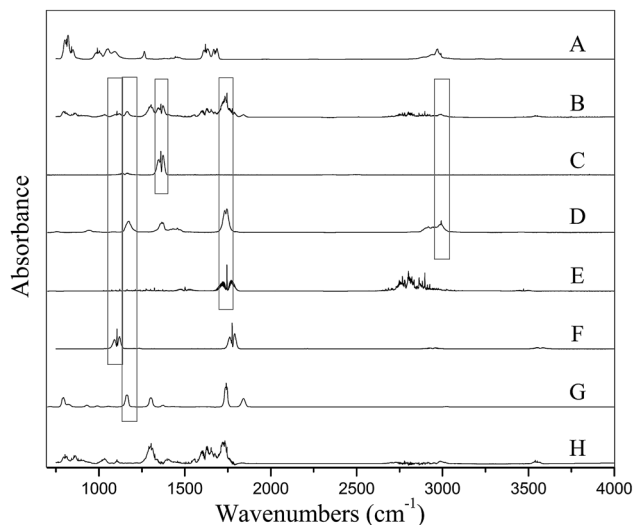
Fig. 3 Trace A shows the IR spectrum for a mixture of 2butSH and methyl nitrate (CH_3ONO) in air acquired before irradiation and the trace B shows the residual spectrum after irradiation and subtraction of the 2butSH, CH_3ONO, CO, CO_2 and H_2O abortions. Traces C show the reference spectrum for SO_2, traces D show the reference spectrum of 2-butanone, traces E show the reference spectrum of (HCHO), traces F show the reference spectrum of formic acid (HC(O)OH), traces G show the reference spectrum of peroxyacetyl nitrate (PAN) and H traces show the residual spectrum after to subtract the spectra of the identified compounds. For comparison proposes all spectra were normalized.

secondary reactions. PAN is a product generated from the reaction of the peroxyacetyl radicals and the NO_2 formed in the reaction (3) during the irradiation of CH_3ONO to produce OH radicals. The formation of HC(O)OH is attributed to the reaction of formaldehyde and HO_2 radicals.[42] The concentration–time profiles of the products (Fig. S1 in ESI†) shows that all products observed are primary whereas the delayed formation in the profile of PAN and HC(O)OH show that its formations are secondary in nature. The identified products and the high yield for SO_2 observed in these reactions supports is that H-abstraction of S–H group mechanism is the main reaction step. We could not identified products coming from alkyl thio alkoxy radicals (R(O•)SR) which would be formed if the reaction proceed *via* H-abstraction from the C–H group of the alkyl chain of the thiol. The unidentified absorptions in the residual spectrum are due to products from the H-abstraction on the alkyl chain of the thiol like thio-acetic acid (CH_3COSH) or thio-propanoic acid (CH_3CH_2COSH) or methyl nitrate (CH_3ONO_2) formed by the reaction of residual methyl nitrite (CH_3ONO) with a alkyl peroxy radical (ROO•). The absorptions bands also could be generated by peroxy nitrate compounds formed through secondary reaction of the main products. Unfortunately, no reference spectra of these compounds are available to compare with our experimental results. However, simulated spectra was used to check if the unidentified bands in the residual spectrum belong to these compounds (see ESI†).

Once identified the reactions products, these were quantified using the reference spectra and the IR cross sections of the

following bands (2972 cm⁻¹) for 2butSH, (1361 cm⁻¹) for SO_2 and (2992 cm⁻¹) for 2-butanone. Plots of the arising concentrations of reaction products *versus* the loss of 2butSH are shown in Fig. 4. The plots results in a straight line, from the least square analysis of the slopes of plots yields (81 ± 2)%, and (42 ± 1)% have been obtained for SO_2 and 2-butanone, respectively. We do not calculate yields PAN because is a secondary product and for formaldehyde and HC(O)OH due that the formaldehyde (HCHO) is also formed as a secondary product from the CH_3ONO photolysis *via* reaction (2) and our experimental conditions do not allow us to discriminate the reaction of source. To best of our knowledge there are no previous product studies of the reaction OH-initiated oxidation of alkyl thiols. Hence, this is the first reported product distribution study of the reaction of OH radicals with 2-butanethiol.

3.2.2 2-Butanethiol + Cl oxidation. Fig. 5 shows the typical spectrum taken during the product identification experiments of the reactions of 2butSH and Cl atoms. Trace A shows an IR spectrum of 2butSH and Cl_2 in air before irradiation. Trace B shows the IR spectra obtained at the end of reaction and after to subtract the absorption due 2butSH that remained unreacted. Traces C, D and E are the reference spectra for SO_2, 2-butanone and HCl, respectively. The residual spectrum after subtraction of the spectra of the identified products is show in trace F. Apart from these primary products, no other products like formaldehyde or acetaldehyde were identified. As in the OH oxidation the unidentified bands could be consequence of absorptions of minor products of secondary reactions or sulfur containing compounds formed from the H-abstraction on the C–H groups in the alkyl chain of the thiol. The reference spectra and the IR cross sections calculations were made in the following bands (2972 cm⁻¹) for 2butSH, (1361 cm⁻¹) for SO_2 and (1745 cm⁻¹) for 2-butanone. The concentration–time profiles of SO_2 and 2-butanone show that both are primary (see Fig. S2 of the ESI†). The yields obtained, from the least square analysis of the slopes
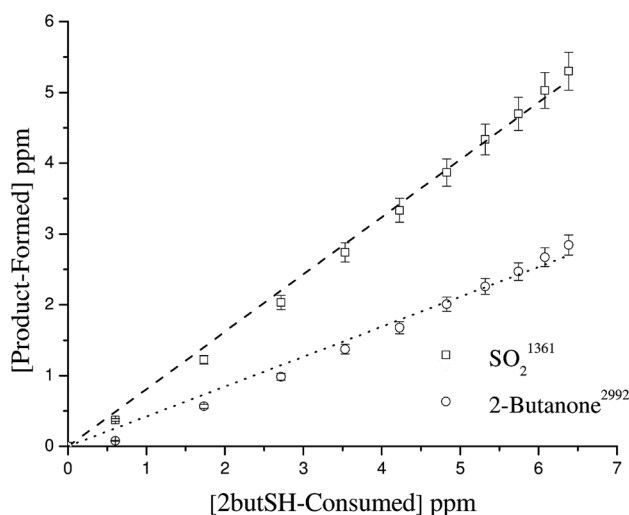

Fig. 4 Plot of the products concentrations of SO_2 and 2-butanone as function of reacted 2butSH with OH radicals at atmospheric pressure of synthetic air and 298 K.
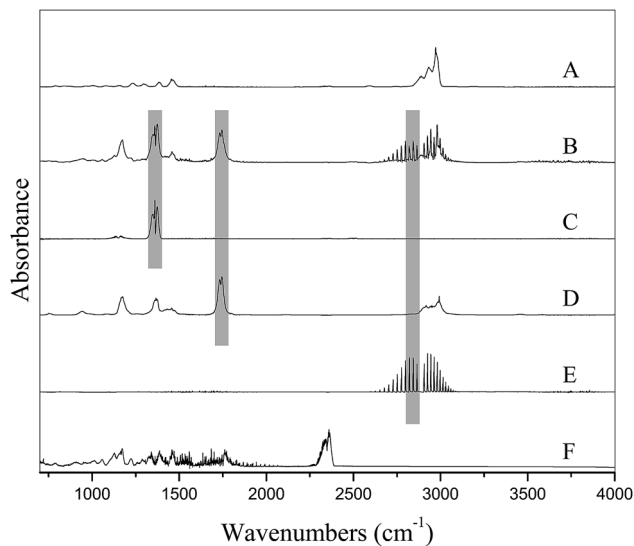
Fig. 5 Trace A shows the IR spectrum for a mixture of 2butSH and Cl_2 in air acquired before irradiation and the trace B shows the residual spectrum after irradiation and subtraction of the 2butSH, CO and CO_2 absorptions. Traces C show the reference spectrum for SO_2, traces D show the reference spectrum of 2-butanone, traces E show the reference spectrum of HCl and F traces show the residual spectrum after to subtract the spectrum of the identified compounds. For comparison proposes all spectra were normalized.

of the plots of arising concentration of the products *versus* 2butSH consumed, were: $(59 \pm 2)\%$ and $(39 \pm 2)\%$ for SO_2 and 2-butanone, respectively (Fig. 6). This is the first product yield quantification of the reaction of 2-butSH with Cl atoms. The yields for SO_2 and HCl are in good agreement with previous values reported for the reactions of Cl with alkyl sulfides like dimethyl sulfide, ethyl methyl sulfide and diethyl sulphide (see Table 3). The product yields suggest that, like in the reaction with OH radicals, the H-abstractions of the S–H group is the
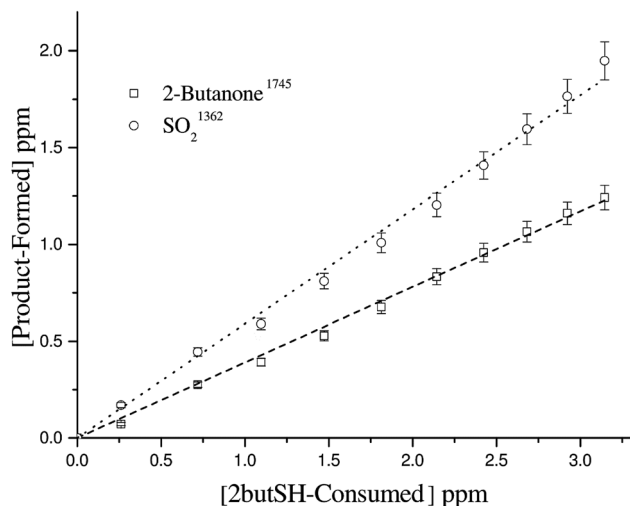

Fig. 6 Plot of the products concentrations of SO_2, 2-butanone as function of reacted 2butSH with Cl atoms at atmospheric pressure of synthetic air and 298 K.

Table 3 Products yields observed in reaction of Cl atoms with 2butSH and comparison for the yield of SO_2 with others VOSC's at atmospheric pressure of synthetic air and 298 K

VOSC's	Product	Yield (%)
$CH_3CH_2CH(SH)$	HCl	97 ± 2
$CH_3{}^a$	$CH_3CH_2C(O)CH_3$	39 ± 2
	SO_2	59 ± 2
$CH_3SCH_3{}^b$	SO_2	39
$CH_3SCH_2CH_3{}^c$	SO_2	55 ± 3
$CH_3CH_2SCH_2CH_3{}^c$	SO_2	52 ± 5

[a] This work. [b] Ref. 9. [c] Ref. 57.

most important degradation channel in agreement with previous kinetic studies for alkyl thiols.[19,21,23,24,43]

3.3 Mechanistic analyses

A proposed H-abstraction of S–H group reaction mechanism based in the products distribution is shown in Fig. 7. The first step is the H-abstraction by OH radical or Cl atoms form the alkyl thiyl radical (RS•). Products of H-abstraction from the C–H groups of the alkyl chain or addition on the S atom could not be identified in our experimental setup. The alkyl thiyl radical reacts further exclusively with molecular oxygen to form the RSOO radicals, which mainly decomposes to SO_2 and an alkyl radical (R•). No evidence of dimerization of the corresponding dialkyl disulfide was observed. Under atmospheric conditions the alkyl radical reacts rapidly with oxygen to form alkyl peroxy radicals, which react with another ROO radical to form alkoxy radicals (RO•) or can react with NO (formed in the CH_3ONO photo-dissociation process).[44]

In particular, in the 2butSH + Cl system, the reaction of the RO radicals with O_2 results exclusively in the 2-butanone and HO_2 radicals pathway. Meanwhile, in the 2butSH + OH system we could identify products of the decomposition of the RO radical pathway. We assume that the formation of peroxy acetyl nitrate, PAN is consequence of the reaction of NO_2 and the peroxyacetyl radical formed. According with above, we suggest that formaldehyde is not only generated in the reaction (2). Our results are in agreement with previous studies focused in the RO radicals fate[45–48] that proposed that the OH-initiated oxidation in presence of NO_X occur *via* the formation of a chemically activated oxy radical which decomposes promptly to yield shorter carbon chain aldehydes. In contrast, the Cl-initiated oxidation does not lead to C–C bond scission, even in the presence of NO[45–48] (see Fig. S3 of ESI†).

3.4 Atmospheric implications

The values of rate coefficients for the reactions of 2butSH with OH radicals and Cl atoms obtained in this work, have been used to calculate the lifetimes in the atmosphere regarding these oxidants. The expression $\tau_X = 1/k_{SH}[X]$ was used to calculate the lifetime of 2butSH in the atmosphere by OH or Cl degradation reactions, where k_{SH} is the rate coefficient and [X] is the OH or Cl average concentration in the troposphere. The average

Fig. 7 Proposed mechanism for the OH radical and Cl atoms oxidation of 2butSH at 298 K and atmospheric pressure of synthetic air. We show the more important possible H-abstraction pathways to form the identified products. X = OH or Cl. The molecules enclosed in the dashed black line rectangle were identified in the reaction with OH radicals and the enclosed in black line rectangles are the identified in the reaction with Cl atoms.

concentrations used were 2×10^6 radicals per cm^3 (ref. 28) and 1×10^4 atoms per cm^3 (ref. 49) for OH radicals and Cl atoms respectively. Once the 2butSH is emitted into the atmosphere mainly through organic matter decomposition it will be removed in the troposphere by gas phase reactions by OH radicals during daytime conditions in about 5.4 hours and by Cl atoms in about 4.6 days. Degradation initiated by Cl atoms will only be important in places where the concentrations is high enough to compete with OH radical degradation, as in the marine boundary layer or high industrialized Mediterranean areas. Is that the Cl atoms. The 2butSH will lead mainly to SO$_2$ in both OH radicals and Cl atoms initiated oxidation. The remaining alkyl radical will react again with molecular oxygen to produce the corresponding carbonyl product. For the Cl atoms degradation, only 2-butanone was identified as a carbonyl product, meanwhile in the OH radicals degradation formaldehyde and peroxyacetyl nitrate were also identified. SO$_2$ is well known to be further oxidized in the atmosphere to H$_2$SO$_{4(g)}$ and SO$_4^{-2}$ and others sulfur acids compounds which can be incorporated into particles to produces cloud condensation nuclei affecting the radiation budget and climate, as well as contributing to episodes of acid rain or increasing the level of particulate material in urban areas.[30,50] These carbonyl products are important in tropospheric chemistry because they may

contribute to secondary aerosol formation, and act as precursor of peroxyacyl nitrates. Even in this work, peroxyacetyl nitrate (PAN) was feasible identified, that is known by its toxicity, plant injury and as an important NO$_X$ reservoir.[51,52]

4 Conclusions

The rate coefficients for the gas phase reaction of 2butSH with OH radicals and Cl atoms have been determined under atmospheric conditions of pressure and temperature. These kinetic data are in good agreement with the reported values for similar alkyl thiols. The rate coefficient values obtained were compared with the values for the homologous alcohols (OH instead of SH group) and it was observed that the rate coefficients for the alkyl thiols in most of cases are bigger. However, the reactions with Cl radicals present similar values in agreement with the less selective nature of Cl atoms. The reactions products of the reactions of 2butSH with both OH radicals and Cl atoms were identified and quantified when possible. In both reactions, the most important reactions product was SO$_2$ formed from the H-abstraction pathway of the S–H group. Further oxidation of the RS$^{\bullet}$ radical with O$_2$ will lead to the C–S bond breaking (Fig. 7). For the OH reactions the identified carbonyl products were 2-butanone, formaldehyde, formic acid and peroxyacetyl nitrate.

No reactions products were identified from C–C breaking bond in the reactions with Cl atoms and only the 2-butanone was identified. The yields for SO_2 and 2-butanone were obtained for both reactions, and the yield for HCl formations for the reaction with Cl atoms are in good agreement with previous work and supports that the reactions proceed *via* H-abstraction on the S–H group of the thiol. Once in the atmosphere, 2butSH will be degraded in a few hours by the OH radical or Cl atoms in places with high concentrations of this chlorine species as marine regions or industrialized continental areas.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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