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

Alejandro L. Cardona, Rodrigo G. Gibilisco, María B. Blanco, Peter Wiesen and Mariano Teruel

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: \( k_{\text{OH}} = (2.58 \pm 0.21) \times 10^{-11} \text{ cm}^3 \text{ per molecule per s} \) and \( k_{\text{Cl}} = (2.49 \pm 0.19) \times 10^{-10} \text{ cm}^3 \text{ per molecule per s} \). 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. \( \text{SO}_2 \) 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 \( \text{SO}_2 \) and 2-butanone, respectively. For the reactions of 2-butanethiol with Cl atom, yields of \( \text{SO}_2 \) 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.\(^1\)–\(^3\) 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\(^4\) due to high contents of organic matter and moisture. Other anthropogenic sources of VOSCs include landfill facilities\(^4\) heavy polluted rivers and creeks.\(^5\) All these sources contribute to the rising concentrations of VOSCs in the air of cities with high population density.\(^7\)

The main and most studied VOSCs are \( \text{H}_2\text{S}, \text{CS}_2 \) and dimethyl sulfide (DMS).\(^8\)–\(^11\) However, in recent years, alkyl thiols have aroused great interest, especially because of the experimental evidence about their presence in various environmental systems.\(^12\)–\(^14\) 2-Butanethiol was detected in samples of air from sewage treatment tanks of chemical petroleum, geothermal areas, muddy beach water and wastewater treatment plants.\(^1\)\(^5\)–\(^1\)\(^8\)

There are several experimental and theoretical studies of the reactions of alkyl thiols with Cl atoms and OH radicals.\(^1\)\(^9\)–\(^2\)\(^7\) 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\(^2\)\(^8\) and even in the mid-continental areas due to the presence of CINO\(_2\) precursor at significant levels, as reported in field measurement observations on regions remote from the coastline.\(^2\)\(^9\)

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.\(^3\)\(^)\(^3\)\(^0\)\(^3\)\(^1\) Some authors discussed the role of the VOSC in atmospheric chemistry as primary irritant and ubiquitous offensive odor pollutants with very low...
sensory thresholds.\textsuperscript{3,4,6} Friedman \textit{et al.}\textsuperscript{22} proposed that even a small anthropogenic perturbation of SO\textsubscript{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.\textsuperscript{23} 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.\textsuperscript{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.\textsuperscript{24} 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 ≤ \(\lambda\) ≤ 450 nm, \(\lambda_{\text{max}} = 360\) 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\textsuperscript{−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 based in the assumption that both 2butSH and reference compounds (R) in the following way:

\[
2\text{butSH} + \text{Cl}_2 \rightarrow \text{products}
\]

The relative rate technique was used to obtain the rate coefficients of the title reactions. In steady-state 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:

\[
\ln\left(\frac{[\text{2butSH}]_0}{[\text{2butSH}]_t}\right) = \frac{k_2}{k_6} \ln\left(\frac{[\text{R}]_0}{[\text{R}]_t}\right)
\]

Plots of ln([2butSH]\textsubscript{0}/[2butSH]\textsubscript{t}) versus ln([R]\textsubscript{0}/[R]\textsubscript{t}), should yield straight lines with slope \(k_2/k_6\), where [2butSH]\textsubscript{0}, [R]\textsubscript{0}, [2butSH]\textsubscript{t} and [R]\textsubscript{t} are the concentrations of 2butSH and reference compounds before irradiation and at time \(t\), respectively, and \(k_2\) 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 react-
ants 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 radi-
cals 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 coeffi-
cients of the reference compounds. However, a comparison of the rate coefficients
with OH radicals and Cl atoms 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
for the reactions of 2butSH with OH radicals, as reference
compounds, and 2-methyl-propene and propene as reference
compounds.

We can notice that the value of $k_{\text{Cl}}$ is almost an order of
magnitude larger than the value for $k_{\text{OH}}$. This may mean, that
the atmospheric degradation with chlorine atoms could be
important, if Cl atoms concentrations are significant. The re-
ported values for $k_{\text{OH}}$ are bigger than the obtained in this study
($\approx 3.8 \times 10^{-11}$ cm$^3$ 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 reac-
tants that those used in this study (Table 1).

On the other hand, the value $k_{\text{Cl}}$ 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

\begin{align*}
(\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{OH} & \rightarrow \text{products} \quad (8) \\
\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{OH} & \rightarrow \text{products} \quad (9) \\
(\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{Cl} & \rightarrow \text{products} \quad (10) \\
\text{CH}_3\text{CH}=\text{CH}_2 + \text{Cl} & \rightarrow \text{products} \quad (11)
\end{align*}

where $k_8$ (5.14 ± 1.03) \times 10^{-11}$, $k_9$ (6.39 ± 1.28) \times 10^{-11}$,$^3$ $k_{10}$
(3.40 ± 0.28) \times 10^{-10}$ (ref. 38) and $k_{11}$ (2.64 ± 0.21) \times 10^{-11}$ (ref.
38). All values are expressed in cm$^3$ 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:

\begin{align*}
k_{\text{OH}} &= (2.58 \pm 0.55) \times 10^{-11} \text{ cm}^3 \text{ per molecule per s} \\
k_{\text{Cl}} &= (2.49 \pm 0.70) \times 10^{-10} \text{ cm}^3 \text{ per molecule per s}
\end{align*}

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.
In this study, the value reported for CH₃CH₂CH₂CH₂SH, is lower than its homologous alcohol, was obtained at reduced pressure, 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.

### 3.2 Reaction products study

Further experiments were made to investigate the mechanism and the product distribution of OH radicals and CI 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 (CH₃ONO) in air acquired before irradiation and trace B shows the spectrum after irradiation and subtraction of the 2butSH and CH₃ONO absorptions. Traces C, D, E, F and G show the reference spectra for SO₂, 2-butane, formaldehyde (HCHO), formic acid (HC(O)OH) and peroxyacetil 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. SO₂, 2-butane and HCHO are the main primary products identified. PAN and HC(O)OH are formed from

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

| Reaction | Reference | $k_{2butSH}/k_{reference}$ | $k_{2butSH}$
|----------|-----------|----------------------------|-----------------
| CH₃CH₂CH(SH)CH₃ + OH | (CH₃)₂C==CH₂ | 0.540 ± 0.001 | (2.78 ± 0.28) × 10⁻¹¹ |
| CH₃CH₂CH₂CH₂CH₂SH + Cl | (CH₃)₂C==CH₂ | 0.634 ± 0.002 | (2.58 ± 0.55) × 10⁻¹¹ |

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

<table>
<thead>
<tr>
<th>Alkyl group</th>
<th>R = OH</th>
<th>R = SH</th>
<th>R = OH</th>
<th>R = SH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃R</td>
<td>0.10 ± 0.02⁸</td>
<td>3.60 ± 0.40⁹</td>
<td>0.56 ± 0.06¹⁰</td>
<td>2.0 ± 0.34¹⁰</td>
</tr>
<tr>
<td>CH₃CH₂R</td>
<td>0.35 ± 0.05⁸</td>
<td>4.50 ± 0.50⁹</td>
<td>1.01 ± 0.06¹⁰</td>
<td>1.9 ± 0.20¹⁰</td>
</tr>
<tr>
<td>CH₃CH₂CH₃R</td>
<td>0.55 ± 0.04⁸</td>
<td>3.20 ± 0.60⁹</td>
<td>1.49 ± 0.07¹⁰</td>
<td>2.57 ± 0.66¹⁰</td>
</tr>
<tr>
<td>(CH₃)₂CH₄R</td>
<td>0.58 ± 0.08⁸</td>
<td>3.90 ± 0.40⁹</td>
<td>0.84 ± 0.04¹⁰</td>
<td>2.70 ± 0.60¹⁰</td>
</tr>
<tr>
<td>CH₃CH₂CH₃CH₃R</td>
<td>0.86 ± 0.07⁸</td>
<td>5.60 ± 0.40⁹</td>
<td>2.04 ± 0.14¹⁰</td>
<td>2.80 ± 0.40¹⁰</td>
</tr>
<tr>
<td>CH₃CH₂CH₂(CH₃)₂R</td>
<td>0.88 ± 0.15⁸</td>
<td>2.58 ± 0.53⁹</td>
<td>1.70 ± 0.14¹⁰</td>
<td>2.49 ± 0.20¹⁰</td>
</tr>
</tbody>
</table>

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| \(a\) 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. |
formed by the reaction of residual methyl nitrite (CH$_3$ONO) with chain of the thiol like thio-acetic acid (CH$_3$COSH) or thio-trum are due to products from the H-abstraction on the alkyl propanoic acid (CH$_3$CH$_2$COSH) or methyl nitrate (CH$_3$ONO$_2$) for SO$_2$ observed in these reactions supports is that H-abstraction from the C-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$_3$COSH) or thio-propanoic acid (CH$_3$CH$_2$COSH) or methyl nitrate (CH$_3$ONO$_2$) formed by the reaction of residual methyl nitrite (CH$_3$ONO) 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 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$_3$ONO 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 thios. 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
of the plots of arising concentration of the products versus 2butSH consumed, were: (59 ± 2)% and (39 ± 2)% for SO2 and 2-butane, respectively (Fig. 6). This is the first product yield quantification of the reaction of 2-but SH with Cl atoms. The yields for SO2 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 most important degradation channel in agreement with previous kinetic studies for alkyl thiols.\textsuperscript{19,21,23,24,41}

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 thyl radical (RS\textsuperscript{•}). 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 thyl radical reacts further exclusively with molecular oxygen to form the RSOO radicals, which mainly decompose to SO2 and an alkyl radical (R\textsuperscript{•}). 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\textsuperscript{•}+), or can react with NO (formed in the CH\textsubscript{3}ONO photo-dissociation process).\textsuperscript{44}

In particular, in the 2butSH + Cl system, the reaction of the RO radicals with O\textsubscript{3} results exclusively in the 2-butane and HO\textsubscript{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\textsubscript{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\textsuperscript{45-48} that proposed that the OH-initiated oxidation in presence of NO\textsubscript{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\textsubscript{X}\textsuperscript{45-48} (see Fig. S3 of ESI\textsuperscript{†}).

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 $\tau_X = 1/k_{\text{rate}}[X]$ was used to calculate the lifetime of 2butSH in the atmosphere by OH or Cl degradation reactions, where $k_{\text{rate}}$ is the rate coefficient and $[X]$ is the OH or Cl average concentration in the troposphere. The average

![Fig. 5](image1.png)  
**Fig. 5** Trace A shows the IR spectrum for a mixture of 2butSH and Cl\textsubscript{2} in air acquired before irradiation and the trace B shows the residual spectrum after irradiation and subtraction of the 2butSH, CO and CO\textsubscript{2} absorptions. Traces C show the reference spectrum for SO2, traces D show the reference spectrum of 2-but SH and Cl\textsubscript{2} radicals. The average concentration in the troposphere. The average

![Fig. 6](image2.png)  
**Fig. 6** Plot of the products concentrations of SO2, 2-butane as function of reacted 2-but SH with Cl atoms at atmospheric pressure of synthetic air and 298 K.

<table>
<thead>
<tr>
<th>VOSC’s Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{3}CH\textsubscript{2}CH(SH)</td>
<td>HCl</td>
</tr>
<tr>
<td>CH\textsubscript{3}CH\textsubscript{2}C(O)CH\textsubscript{3}</td>
<td>SO2</td>
</tr>
<tr>
<td>CH\textsubscript{3}SCH\textsubscript{2}CH\textsubscript{3}</td>
<td>SO2</td>
</tr>
<tr>
<td>CH\textsubscript{3}SCH\textsubscript{2}CH\textsubscript{3}</td>
<td>SO2</td>
</tr>
<tr>
<td>CH\textsubscript{3}SCH\textsubscript{2}CH\textsubscript{3}</td>
<td>SO2</td>
</tr>
</tbody>
</table>

\textsuperscript{a} This work. \textsuperscript{b} Ref. 9. \textsuperscript{c} Ref. 57.
concentrations used were $2 \times 10^6$ radicals per cm$^3$ (ref. 28) and $1 \times 10^4$ 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$_4$ 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. 48,50 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.

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$^\cdot$ 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.

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.
No reactions products were identified from C–C breaking bond in the reactions with Cl atoms and only the 2-butanoic acid was identified. The yields for SO₂ and 2-butanoic acid 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.

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