**Atmospheric
Chemistry
and Physics**

Reactions of isoprene and sulphoxy radical-anions – a possible source of atmospheric organosulphites and organosulphates

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Abstract. Transformation of isoprene coupled with auto-oxidation of S^{IV} in aqueous solutions was studied experimentally and by chemical-kinetic modelling over a broad range of solution acidities (pH=3–9) to complement the research on aqueous-phase and heterogeneous transformation of isoprene reported recently by many laboratories. Isoprene significantly slowed down the auto-oxidation in acidic and basic solutions, and accelerated it slightly in neutral solutions. Simultaneously, production of sulphate ions and formation of solution acidity were significantly reduced. Formation of sulphite and sulphate derivatives of isoprene - sulphurous acid mono-(2-methyl-4-oxo-but-2-enyl) ester (m/z=163), sulphurous acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester (m/z=165), sulphuric acid mono-(2-methyl-4-oxo-but-2-enyl) ester (m/z=179), sulphuric acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester (m/z=181), and possible structural isomers of these species – was indicated by electrospray ionisation mass spectrometric analysis of post-reaction mixtures. The experimental results were explained by changes in a subtle quantitative balance of three super-imposed processes whose rates depended in different manner on the acidity of reacting solutions – the scavenging of sulphoxy radical-anions by isoprene, the formation of sulphoxy radical-anions during further reactions of isoprene radicals, and the auto-oxidation of S^{IV} itself. A chemical mechanism based on this idea was explored numerically to show good agreement with experimental data. In basic and neutral solutions, the model overestimated the consumption of isoprene, probably because reactions of primary sulphite and sulphate derivatives of isoprene with sulphoxy radical-anions were not included. Interaction of isoprene with sulphur(IV) species and oxygen can possibly result in formation of new organosulphate and organosulphite components of atmospheric aerosols and waters, and influence the distribution of reactive sulphur and oxygen species in isoprene-emitting organisms exposed to S^{IV} pollutants.

1 Introduction

Isoprene (C_5H_8) and sulphur dioxide (SO_2) are important trace components of the atmosphere that are emitted from biogenic and anthropogenic sources (Georgii and Warneck, 1999; Sharkey et al., 2007). Sulphur dioxide is also produced directly in the atmosphere, for instance by oxidation of dimethylsulphide (Barnes et al., 2006). The recognised fate of SO_2 is conversion to sulphuric acid and sulphates, in the gas-phase, heterogeneous or multiphase processes (Seinfeld and Pandis, 2006). On the other hand, isoprene is quickly oxidised in the gas phase by radicals (OH, NO_3) and by ozone, to several primary and many secondary products, such as methacrolein and methylvinyl ketone or methylglyoxal and organic nitrates, respeicvely (LeBras and the LACTOZ Steering Group, 1997; Fan and Zhang, 2004; Paulot et al., 2009; Taraborrelli et al., 2008).

The discovery of tetrols in ambient aerosol samples collected in Amazon rainforest and boreal K-Puszta forest (Claeys et al., 2004a,b) spawned intensive research on formation of secondary organic aerosol (SOA) in heterogeneous and multiphase reactions of isoprene. For review of this research see (Rudziński, 2006, 2008). In summary, numerous experiments in simulation chambers, unseeded or seeded with ammonium sulphate particles, showed isoprene induced formation of aerosol that contained such compounds as methyltetrols, C_5 alkene triols, 2-methylglyceric acid,

glyoxal, methylglyoxal, acetals and hemiacetals, organosulphates and organonitrates, as well as oligomers of some of these (Surratt et al., 2007a,b, 2008). Yield and composition of aerosol depended on the presence of NO_x or SO_2 in the gas phase, or H_2SO_4 added to acidify the seed particles.

In particular, sulphuric acid and sulphur dioxide increased the yields of aerosol (Jang et al., 2002; Limbeck et al., 2003; Kleindienst et al., 2006; Surratt et al., 2007b). Sulphuric acid alone promoted the heterogeneous and aqueous formation of isoprene derivatives containing sulphate functional groups. Formation of these organosulphates was originally explained by direct reaction of the acid with products of isoprene oxidation such as aldehydes and polyols (Liggio et al., 2005; Surratt et al., 2007a). However, a recent experimental study showed direct esterificaton of alcohols was not feasible kinetically (Minerath et al., 2008). Reactions of glyoxal on ammonium sulphate aerosol produced glyoxal sulphate only upon irradiation (Galloway et al., 2008), which likely could initiate the formation of sulphate radical-anions. On the other hand, isoprene was shown to inhibit the aqueous-phase auto-oxidation of dissolved SO_2, or rather sulphite ions (Rudziński, 2004). The suggested mechanism of inhibition included direct reaction of isoprene with sulphate radical-anions, which led to formation of sulphate esters of isoprene derivatives.
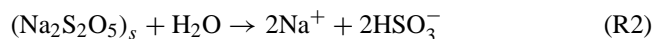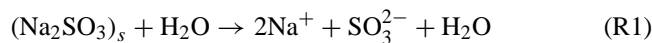
The aim of this work was to show that aqueous reactions of sulphoxy radical-anions with isoprene can produce sulphur-containing derivatives of isoprene, and to show how these reactions depend on and influence the acidity of aqueous solutions during oxidation of dissolved S^{IV} species (sulphur dioxide, sulphite ions) to S^{VI} species (sulphuric acid, sulphate ions).

2 Experimental

2.1 Method

The experimental method we used to study the transformation of isoprene coupled with auto-oxidation of S^{IV} catalysed by manganous sulphate was described in detail by Rudziński (2004). We used a well stirred glass reactor of $0.785\,dm^3$ volume, closed with a Teflon cover and thermostatted within a water jacket. The reactor was operated homogenously (no gas phase was present), and in a batch manner. Each experimental run was prepared by filling the reactor with aqueous solution of manganese catalyst and oxygen, and adding an aliquot of aqueous solution of isoprene. Then, the reactor was sealed and the run was started by injecting an aliquot of aqueous solution of sodium sulphite. This solution was prepared from Na_2SO_3 and $Na_2S_2O_5$ used in different proportions in order to obtain the desired initial acidities of the reacting mixtures (Reactions R1–R3). Only for the lowest

initial acidity (pH=2.9), we additionally acidified the mixture with a small amount of dilute sulphuric acid.

$$(Na_2SO_3)_s + H_2O \rightarrow 2Na^+ + SO_3^{2-} + H_2O \qquad (R1)$$

$$(Na_2S_2O_5)_s + H_2O \rightarrow 2Na^+ + 2HSO_3^- \qquad (R2)$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-} \qquad (R3)$$

The variables recorded in each experimental run included pH, concentration of dissolved oxygen, temperature and high resolution UV spectra of reacting solutions. The pH and concentration of oxygen were measured continuously, using a Ross Ultra glass combination pH electrode and a 525A+ pH-meter from Thermo Electron, and a 9708-99 oxygen probe (Clark type) with 920 pH-meter from Orion (now also Thermo Electron). The oxygen electrode was calibrated before each experiment against the electronic zero and the local atmospheric pressure, using a built-in circuitry. The concentration of dissolved oxygen was read directly from the pH-meter, in ppmO_2. Voltage signals from both pH-meters were recorded every 0.1 s, and converted to pH and oxygen concentration in $mol\,dm^{-3}$, using a computer system equipped with a M6281 data acquisition card and a LabView application, both from National Instruments. The UV spectra were recorded periodically with a Jasco V570 spectrophotometer (0.2 nm bandwidth, 0.5 nm data pitch, 1 cm light path), using a closed sampling loop constructed from a T valve, a syringe and a Hellma Suprasil cell. Temperature in the reactor was measured with a mercury thermometer. Post-reaction solutions were analysed off-line, and in negative ion mode using an API 365 triple quadrupole mass spectrometer with electrospray ionisation from Applied Biosystems. The samples were taken directly after each experiment, using a gas-tight syringe to prevent the access of air, and diluted with methanol before injection to the MS apparatus.

Concentrations of isoprene, sulphite ions and bisulphite ions in the reacting solutions were obtained from the recorded UV spectra by subtraction of reference spectra of these species. The accuracy of determination of subtraction coefficients was better than 12%. The reference spectra and the analysis of subtraction errors were given in (Rudziński, 2004).

2.2 Chemicals

Most of chemicals were purchased from Merck and used without further purification: C_5H_8 for synthesis grade, stabilised with 100 ppm of 4-*tert*-butylpyrocatechol, Na_2SO_3, $Na_2S_2O_5$ and $MnSO_4\times H_2O$ ACS pro analysi grade. Sulphuric acid, pro analysis grade, was obtained from CHEMAN. Buffer standards used for daily calibration of pH electrodes were from Thermo Electron.

All solutions were prepared using the Milli-Qplus Millipore water. Oxygen was dissolved in water by equilibration with atmospheric air. Liquid isoprene was dissolved in water with the aid of an ultrasonic bath.

Table 1. Experimental conversion ratios in transformation of iso-
prene coupled with auto-oxidation of S^{IV}.

Initial pH	$\Delta\left[S^{IV}\right]/\Delta\left[O_2\right]$	$\Delta\left[C_5H_8\right]/\Delta\left[S^{IV}\right]$
8.3	1.53	0.21
7.7	1.28	0.25
7.0	1.52	0.25
5.8	1.63	0.40
4.0	1.61[a]	1.21[a]

[a] the values have inreased uncertainty, because conversion of each
reactant was lower than 1%.

3 Results and discussion

All experiments were carried out at 25.0±0.2°C. Initial con-
centrations of reactants were set to $(0.950\pm0.020)\times10^{-3}$
$mol\,dm^{-3}$ (S^{IV}), $(0.250\pm0.030)\times10^{-3}\,mol\,dm^{-3}$ (O_2),
$(0.117\pm0.050)\times10^{-3}$ $mol\,dm^{-3}$ (C_5H_8), 1.0×10^{-5}
$mol\,dm^{-3}$ $(MnSO_4)$. The initial acidity of reacting solutions
varied from pH=2.9 to 8.5. Each experiment with isoprene
was paired with another experiment carried out at practically
the same conditions but without isoprene. Figure 1 shows
sample time traces of reactant concentrations and pH,
obtained from a single experimental run in neutral solution,
with isoprene present.

3.1 Influence of isoprene on auto-oxidation of S^{IV}

Auto-oxidation of S^{IV} catalysed by transition metals and
undisturbed by addition of foreign substances is charac-
terised by a fixed ratio of S^{IV} conversion to oxygen con-
version, which reflects the 2:1 stoichiometry of the overall
reaction (Reaction R4). In the presence of isoprene, the con-
version ratio dropped to lower values, due to formation of
oxygenated derivatives of isoprene (Table 1, see also mecha-
nism in Sect. 4, Figs. 7–9).

$$2Na_2SO_3 + O_2 \xrightarrow{MnSO_4} 2Na_2SO_4 \qquad (R4)$$

Our previous work showed that isoprene slowed down
the auto-oxidation of S^{IV} in solutions of pH ≥8 (Rudziński,
2004). Here, we confirmed this observation for higher con-
centrations of isoprene, and extended the experiment to neu-
tral and acidic solutions (pH=3÷8).

We found that isoprene slowed down the auto-oxidation
of S^{IV} in acidic and basic solutions (pH$_o$< 7 and pH$_o$>8),
but accelerated it in neutral solutions (pH$_o$=7÷8). Figures 2
and 3 compare time traces of the dimensionless concentration
of oxygen (x_{O2}=[O_2]/[O_2]$_o$) obtained from experiments in
acidic and basic solutions, with and without isoprene added
(red and cyan lines, respectively). In all these cases, isoprene
slowed down the auto-oxidation. In solutions of pH<5, the
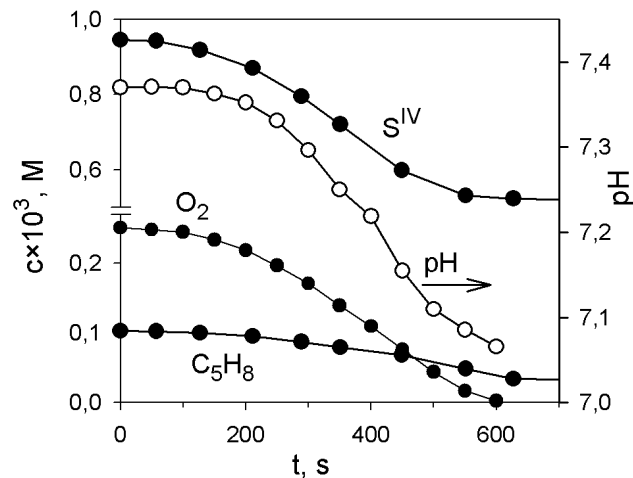uninhibited auto-oxidation was so slow itself, that isoprene

Fig. 1. Transformation of isoprene coupled with auto-oxidation of
S^{IV} – time traces of reactant concentrations and pH obtained from
an experiment in neutral solution (S^{IV} is sum of HSO_3^- and SO_3^{2-}
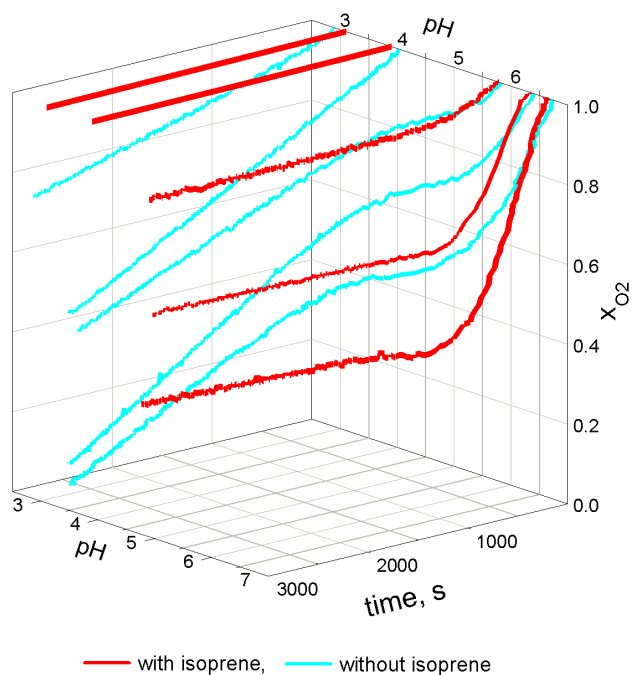ions).

Fig. 2. Inhibition of S^{IV} auto-oxidation by isoprene in acidic solu-
tions – time traces of dimensionless concentration of oxygen.

could stop it almost completely. On the contrary, Fig. 4
shows that in all experiments in neutral solutions, isoprene
accelerated the auto-oxidation. The diverse influence of iso-
prene could result from subtle changes in a quantitative bal-
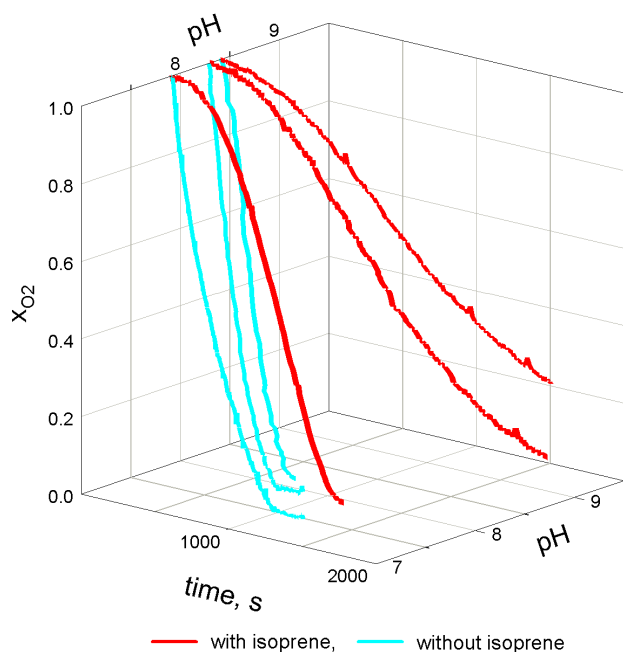ance of three superimposed processes whose rates depended

Fig. 3. Inhibition of S^{IV} auto-oxidation by isoprene in basic solutions – time traces of dimensionless concentration of oxygen.

Fig. 4. Acceleration of S^{IV} auto-oxidation by isoprene in neutral solutions – time traces of dimensionless concentration of oxygen.

in a different manner on the acidity of reacting solutions – the scavenging of sulphoxy radicals by isoprene, the formation of sulphoxy radicals during further transformation of isoprene, and the auto-oxidation of S^{IV} itself. The chemical mechanism utilising this concept was discussed in Sect. 4.

Figures 2–4 show that in all experiments, the addition of isoprene reduced the acidification of reacting solutions. During uninhibited auto-oxidation of S^{IV}, the solutions were acidified due to changes in the acid-base dissociation balance that took place when sulphite and bisulphite ions were converted into sulphate ions. Isoprene always reduced this acidification markedly, or even reversed it in experiments starting at pH>8.2. This influence was a natural consequence of slower auto-oxidation of S^{IV}, but also reflected the formation of isoprene derivatives capable of associating with free protons in solutions.

3.2 Transformation of isoprene

The analysis of UV spectra of reacting solutions showed that in all experiments isoprene decayed proportionally to the decay of sulphite. The ratio of these conversions ranged from 0.21 to 0.40, and to 1.21, the latter value being rather uncertain as calculated from conversions lower than 1% (Table 1). In neutral and slightly acidic solutions, we saw weak light absorption by non-sulphate reaction products, with a broad peak at 240 nm (Fig. 5). The peak was positioned at longer wavelengths than the 225 nm peak of isoprene (Rudziński,
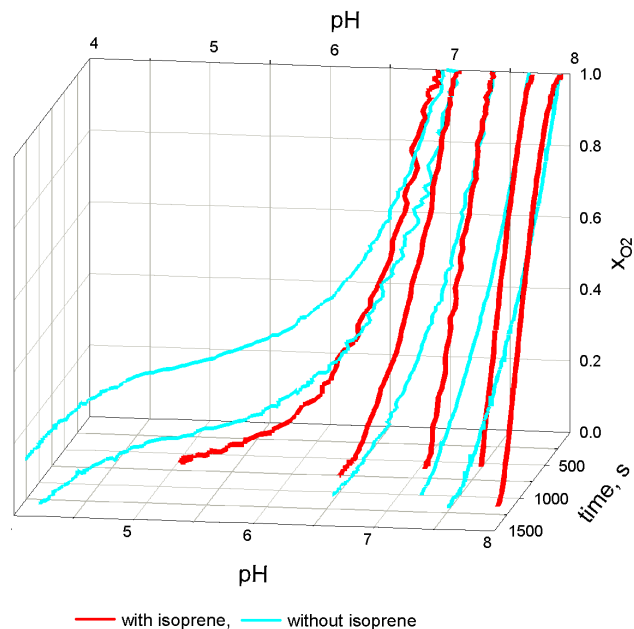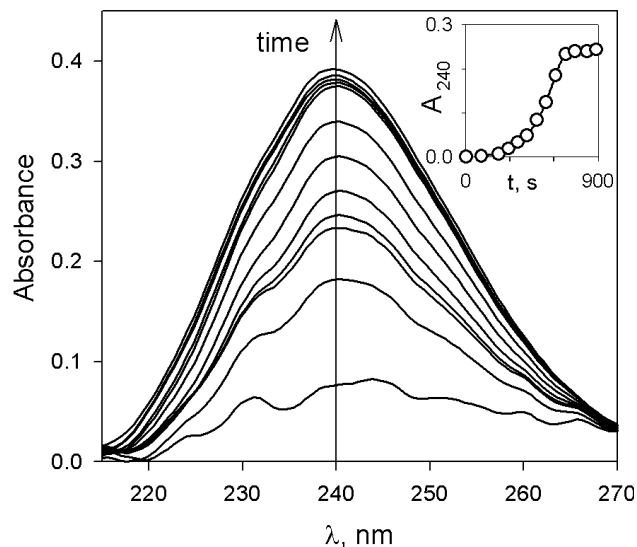

Fig. 5. UV absorption spectra of products of isoprene transformation coupled with S^{IV} auto-oxidation in an experiment starting at pH=6.6. Inset shows the time trace of absorbance at 240 nm.

2004), and close to the 239 nm peak of the unsaturated aldehyde 3-methylbut-2-enal, $(CH_3)_2C=CH-CHO$, calculated using the increment method (Hesse et al., 1997): 207 nm for the base structure $-C=C-CHO$ in methanol+24 nm for two CH_3 groups+8 nm for water replacing methanol as a solvent.

Two structural isomers of this aldehyde had calculated peaks at positions a little more distant: $CH_3CH=C(CH_3)-CHO$ at 237 nm, and $CH_2=C(CH_3)-C(CH_3)O$ at 233 nm. All three carbonyls are similar in structure to possible products of isoprene transformation in our experiments, which additionally contain sulphate or sulphite substituents. We cautiously suggest that spectra in Fig. 5 indicate these products, because the influence of sulphate or sulphite groups on the UV absorption above 200 nm is likely negligible. Unfortunately, other possible products of isoprene transformation, which contain hydroxyl groups instead of carbonyl oxygens, would not absorb the UV light between 200 and 300 nm, and, if present, were invisible to our absorbance measurements.

Electrospray ionisation mass spectra of post-reaction solutions contained peaks of deprotonated molecules that could be attributed to products of isoprene transformation initiated by sulphite and sulphate radical-anions (Fig. 6), such as sulphurous acid mono-(-2-methyl-4-oxo-but-2-enyl) ester (m/z=163), sulphurous acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester (m/z=165), sulphuric acid mono-(2-methyl-4-oxo-but-2-enyl) ester (m/z=179), and sulphuric acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester (m/z=181). Test analyses excluded the possibility of analytical artefacts, showing that the peaks did not appear in spectra of freshly prepared solutions containing isoprene and sodium sulphate or isoprene and sodium sulphite. The compounds shown in Fig. 6 are examples of several structural isomers, which could be produced in our experiments and attributed to the observed MS peaks. A sulphoxy radical can add to double bonds in isoprene at four different positions. Consequently, further reactions can produce five -oxo- isomers

$HO_xSO-CH_2-C(CH_3)=CH-CHO$,
$CH_2=CH-(CH_3)C(OSO_xH)-CHO$,
$CH_2=C(CH_3)-CH(OSO_xH)-CHO$,
$HO_xSO-CH_2-CH=C(CH_3)-CHO$,
$CH_2=C(CH_3)-C(O)-CH_2-OSO_xH$,

and six -hydroxy- isomers

$HO_xSO-CH_2-(CH_3)C(OH)-CH=CH_2$,
$HO_xSO-CH_2-C(CH_3)=CH-CH_2OH$,
$CH_2=CH-(CH_3)C(OSO_xH)-CH_2OH$,
$CH_2=C(CH_3)-CH(OSO_xH)-CH_2OH$,
$HO_xSO-CH_2-CH=C(CH_3)-CH_2OH$,
$CH_2=C(CH_3)-CH(OH)-CH_2-OSO_xH$

for each type of sulphoxy radical involved (x=2 for sulphite radical, and x=3 for sulphate radical). Identification of individual isomers was not possible in this work, and would require higher yields of the products, and commercial or synthesised standards that were not available. However, three of the -oxo- compounds were also indicated by the UV spectra discussed in the previous subsection.

Whatever their exact structure is, the tentatively identified compounds have double carbon-carbon bonds that can react further, for instance with radical species. Saturated organosulphates produced in such reactions would be similar to sulphate esters of methylglyceric acid and 2-methyltetrols
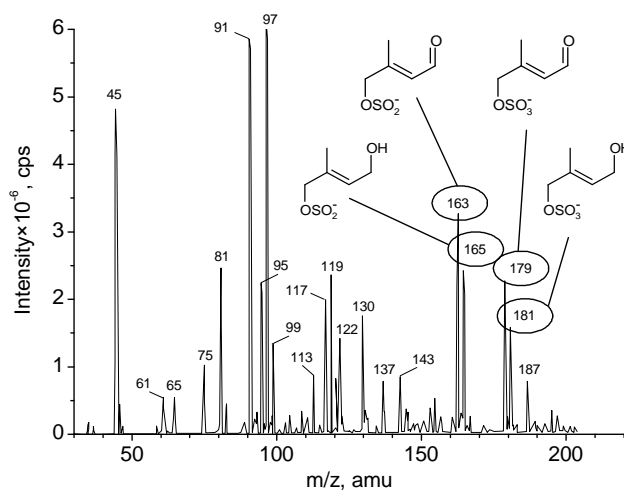

Fig. 6. Peaks corresponding to products of isoprene transformation coupled with auto-oxidation of S^{IV} appeared in negative ion electrospray ionisation mass spectra of post-reaction solutions.

that had been detected in field samples of atmospheric aerosols (Gómez González et al., 2007; Surratt et al., 2007a, 2008).

4 Chemical mechanism and simulation of experiments

Auto-oxidation of S^{IV} catalysed by manganese was studied extensively in the context of both atmospheric chemistry and technology of cleaning the industrial waste gases or waste-waters (Pasiuk-Bronikowska et al., 1992; Berglund and Elding, 1995; Brandt and van Eldik, 1995; Fronaeus et al., 1998; Grgić and Berčič, 2001; Ermakov and Purmal, 2002; Kuo et al., 2006). It is a chain reaction initiated by Mn^{III} and propagated by sulphoxy radical-anions which also regenerate Mn^{III}. In the absence of inhibitors, the chain terminates via several radical-radical reactions.

The chemical mechanism constructed to explain our experiments with transformation of isoprene coupled with auto-oxidation of S^{IV} consisted of three groups of reactions – auto-oxidation of Mn^{II} to Mn^{III} in presence of sulphite or bisulphite ions (Fig. 7), auto-oxidation of sulphite and bisulphite ions (S^{IV}) catalysed by $MnSO_4$ (Fig. 8), and transformation of isoprene initiated by sulphate radical-anions (Fig. 9) or by sulphite radical-anions (not shown, since analogous to the scheme for sulphate radical-anions). The individual reactions in the schemes were identified by specific symbols of the rate constants rather than by cosecutive numbers, to simplify the presentation and provide better mnemonic association. Values of the rate constants used in simulations were collected in Table 2, along with available references.

Table 2. Rate constants used for simulation of chemical mechanism shown in Figs. 7–9.

Constant in Fig. 7	Value $M^{-1} s^{-1}$	Constant in Fig. 8	Value $M^{-1} s^{-1}$	Constant in Fig. 9	Value $M^{-1} s^{-1}$
k_{ass}	1.0×10^{11}	k_{ass}	1.0×10^{11}	k_{s1}[k]	2.19×10^9
k_{dys}[a]	6.75×10^3	k_{dys}[a]	6.75×10^3	k_{s2}	1.0×10^9
k_{kfb}	6×10^6	k_{ib}	1.0×10^3	k_{s3b}	1.0×10^9
k_{kbb}	1	k_{ia}	3.0×10^1	k_{s3a}	1
k_{kfa}	6×10^6	k_{p1}[d]	1.5×10^9	k_{s4b}	1.0×10^9
k_{kba}	1	k_{p21b}[e]	3.25×10^6	k_{s4a}	1.0×10^9
k_{afb}	6	k_{p22b}[e]	9.75×10^6	k_{s5}	$(1 \div 5) \times 10^4$
k_{abb}	1	k_{p21a}[e]	2.5×10^4	k_{s6}[l]	3.5×10^9
k_{afa}	$8 \div 10$	k_{p22a}[e]	7.5×10^4		
k_{aba}	1	k_{p3b}[f]	1.4×10^7	Analogous constants for	
k_{dfb}	6	k_{p3a}[f]	1.4×10^7	reactions of SO_3^- radicals	
k_{dbb}	1	k_{ox11}	3.2×10^6	(not shown in figures)	
k_{dfa}	$8 \div 10$	k_{ox12}	1.2×10^2		
k_{dba}	1	k_{ox2}	1.0×10^6	k_{2s1}	1.0×10^9
k_{o2b}	6	k_{t22}[g]	1.0×10^8	k_{2s2}	1.0×10^9
k_{o2a}	$8 \div 10$	k_{cas}	1.0×10^{10}	k_{2s3b}	5.0×10^4
k_{hpb}[b]	0.19	k_{cdy}[a]	3.98	k_{2s3a}	1.0×10^6
k_{hpa}[c]	3.4×10^7	k_{fb}	7.5×10^3	k_{2s4b}	$(1.2 \div 2.5) \times 10^4$
		k_{fa}	7.5×10^3	k_{2s4a}	5.0×10^4
		k_{t1}[h]	4.0×10^8	k_{2s5}	1
		k_{t21}[i]	1.0×10^7		
		k_{t3}	1.0×10^6		
		k_{t4}[j]	5.0×10^8		

[a] s^{-1}. [b] Drexler et al. (1992). [c] $M^{-2} s^{-1}$, rate=$k_{hpa}[H^+][H_2O_2][HSO_3^-]$, Drexler et al. (1991). [d] Huie and Neta (1984). [e] Huie and Neta (1987). [f] Averaged in CAPRAM. [g] 5.5×10^6 Herrmann et al. (1995), $\sim 2.2 \times 10^8$ Buxton et al. (1996). [h] Waygood and McElroy (1992). [i] 1.3×10^8 Herrmann et al. (1995), 4.8×10^7 Buxton et al. (1996). [j] McElroy and Waygood (1990). [k] Rudziński (2004). [l] 1.7×10^9 Buxton et al. (1996).

4.1 Group 1 – auto-oxidation of Mn^{II} in presence of sulphite or bisulphite ions (Fig. 7)

Chemical-kinetic modeling of our experiments required some mechanism for the initial oxidation of Mn^{II} to Mn^{III} in the presence of sulphite or bisulphite ions. Common reaction pathways suggested in literature included oxidation of Mn^{II} by such impurities as other transition metal ions (Grgić and Berčič, 2001), and several oxidation schemes based on formation of manganese-sulphite complexes and oxygen adducts (Bassett and Parker, 1951; Berglund and Elding, 1995). Here, we used a mechanism first introduced by Rudziński and Pasiuk-Bronikowska (2000), which utilised the idea of formation of μ-peroxo-dimer of metal complexes with organic ligands (Wilkins, 1971; Mimoun, 1980), followed by intramolecular one-electron oxidation of Mn^{II} and decomposition to Mn^{III}, H$_2$O$_2$ and hydroxyl ions (Gubelmann and Williams, 1983). The scheme comprised reversible formation of Mn^{II}-sulphite complexes (k_{kfa}/k_{kba} and k_{kfb}/k_{kbb}), reversible addition of oxygen molecule to this complex followed by intramolecular one-electron oxi-

dation of Mn^{II} (k_{afa}/k_{aba} and k_{afb}/k_{abb}), then formation of dimer from the adduct and the complex (k_{dfa}/k_{dba} and k_{dfb}/k_{dbb}) and intramolecular oxidation of second Mn^{III}, and finally decomposition of the dimer to H$_2$O$_2$ and Mn^{3+} (k_{o2a}/k_{o2b}). Unoxidised sulphite ions were released from the dimer, while oxygen molecule was used to build H$_2$O$_2$, which could oxidise sulphite ions directly to sulphate ions (k_{hpa} and k_{hpb}). Two hydroxyl ions were also formed, which resulted in some alkalisation of the reaction mixture. The oxidation of Mn^{II} could take two parallel paths, one starting with SO$_3^{2-}$ ions and the other – with HSO$_3^-$ ions, the two bound by a reversible association-dissociation reaction (k_{ass}/k_{dys}).

The extent of Mn^{III} auto-oxidation was very minor, and its purpose was to start the auto-oxidation of S^{IV} by supplying the very initial amount of Mn^{3+} in the absence of any other initiator. When the auto-oxidation chain grew longer, Mn^{II} was oxidised back to Mn^{III} in several reactions with sulphoxy radicals and ions. This is exactly why manganese is also called a catalyst of auto-oxidation.
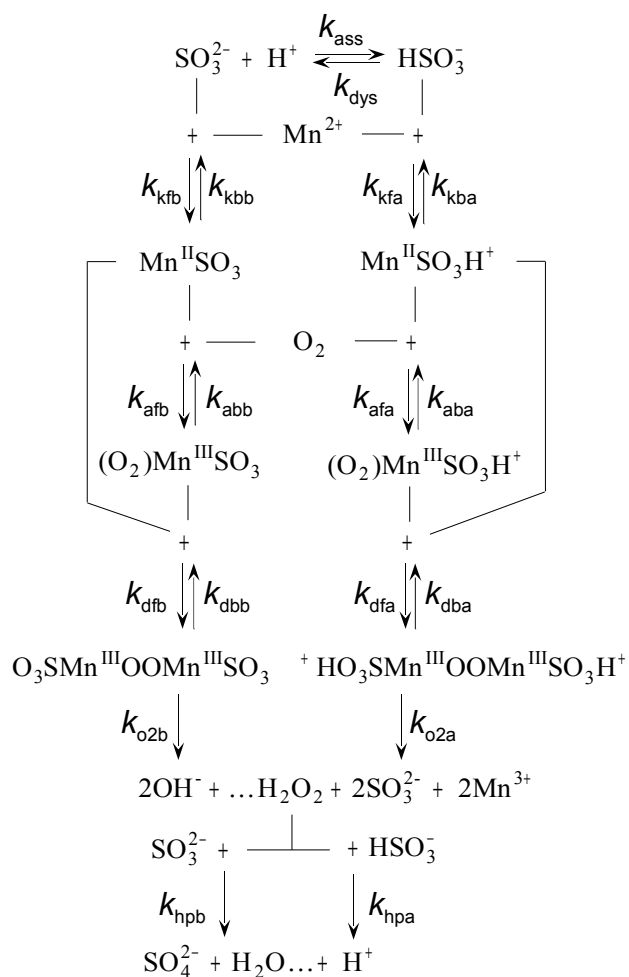
Fig. 7. Mechanism of auto-oxidation of Mn^{II} in the presence of sulphite and bisulphite ions.

4.2 Group 2 – auto-oxidation of S^{IV} catalysed by manganese (Fig. 8)

Chain auto-oxidation of S^{IV} was initiated by formation of sulphite radical-anions in reaction of Mn^{3+} with sulphite or bisulphite ions (k_{ib} and k_{ia}), and proceeded via several propagation steps – formation of peroxymonosulphate radical-anions from sulphite radical-anions and oxygen (k_{p1}), split reactions of peroxymonosulphate radical-anions with sulphite or bisulphite ions that led to formation of peroxymonosulphate ions and regeneration of sulphite radical-anions (k_{p21a} and k_{p21b}), or to formation of sulphate radical-anions and sulphate ions (k_{p22a} and k_{p22b}), and reaction of sulphate radical-anions with sulphite or bisulphite ions, which regenerates sulphite radical-anions (k_{p3a} and k_{p3b}). Peroxymonosulphate ions SO_5^{2-} were reversibly protonated to HSO_5^- ions (k_{cas}/k_{cdy}). Sulphate ions were also produced in reaction of peroxymonosulphate ions with sulphite ions (k_{fa}

and k_{fb}), which could include formation of an intermediate complex that had not been included in the present mechanism. Chain termination occurred via radical-radical reactions (k_{t1}, k_{t21}, k_{t3}, k_{t4}). Reaction of two peroxymonosulphate radical-anions could also regenerate sulphate radical-anions (k_{t22}). The chain initiator, Mn^{3+}, was regenerated in reactions of Mn^{2+} cations with sulphite radical-anions (k_{ox11}), sulphate radical-anions (k_{ox2}) and peroxymonosulphate ions (k_{ox12}).

4.3 Group 3 – transformation of isoprene initiated by sulphoxy radical-anions (Fig. 9)

In this mechanism, isoprene could react with sulphite and sulphate radical-anions. Each radical could add to one of two double bonds of isoprene at any of four locations (1, 2, 3 or 4). We assumed there were no kinetic differences between these additions, so they could be represented by a single reaction for each type of sulphoxy radicals. The final products of isoprene transformation included in the mechanism were the compounds indicated by mass spectra of post-reaction solutions (Fig. 6).

Figure 9 shows the mechanism of isoprene transformation initiated by addition of sulphate radicals (k_{s1}). Alkyl radicals were formed that accepted oxygen molecules to form peroxyalkyl radicals (k_{s2}). The peroxyalkyl radicals could oxidise sulphite (k_{s3b}) or bisulphite ions (k_{s3a}), while turning into alkoxy radicals. The alkoxy radicals reacted with sulphite (k_{s4b}) or bisulphite ions (k_{s4a}) to form a hydroxy derivative of isoprene and to regenerate sulphite radical-anions. In a parallel reaction with oxygen, the alkoxy radicals turn into an oxy derivative of isoprene and produce hydroperoxy radicals (k_{s5}). Hydroperoxy radicals reacted with sulphate radical-anions, producing sulphate ions (k_{s6}).

An analogous scheme (not shown here) was constructed for transformation of isoprene starting with the addition of a sulphite radical-anion to a double bond. The rate constants for the respective reactions were distinguished by adding "2" in the subscript (k_{2s1}, k_{2s2}, k_{2s3a}, k_{2s3b}, k_{2s4a}, k_{2s4b}, k_{2s5}). The isoprene derivatives were similar to those obtained in the transformation initiated by sulphate radical-anions, but contained -OSO_2 substituent groups instead of -OSO_3.

4.4 Simulation of experiments

Basing on the chemical mechanism described above, a corresponding set of ordinary differential equations was constructed and solved using a Mathematica 2.3 package. Reversible reactions were treated kinetically, each one as a pair of independent reactions. Rate constants used for simulations were collected in Table 2. Constants, for which no experimental estimates were available, were adjusted using trial and error guesses.
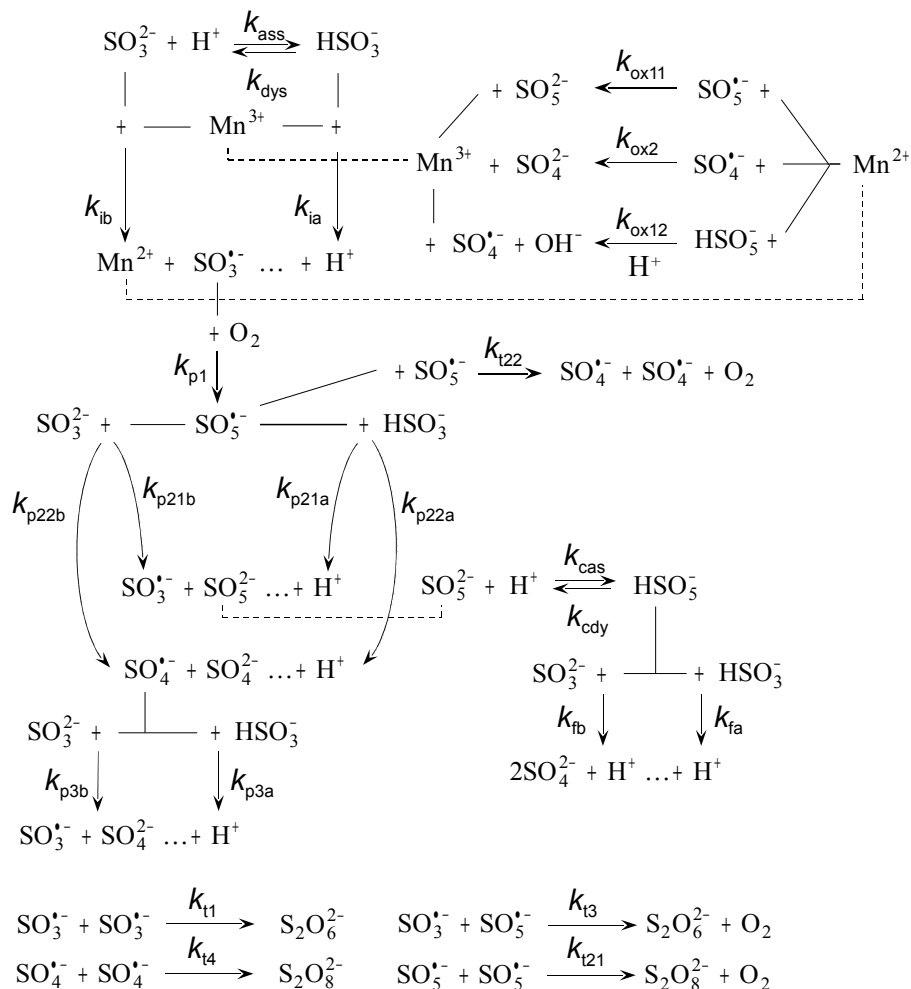
Fig. 8. Mechanism of S^{IV} auto-oxidation catalysed by manganese.

The results of simulation were compared to matching experiments in figures arranged according to the initial values of pH of reacting mixtures. Time traces of reactant concentrations were shown in Figs. 10 and 11, while changes of pH of reacting solutions were shown in Fig. 12. Generally, time traces of S^{IV} and oxygen concentrations were reproduced with good accuracy at all acidities. Consumption of isoprene was simulated quite accurately in acidic solutions, but was overestimated in basic and neutral solutions. The simulation was still accurate qualitatively, reproducing the right shapes of isoprene time traces from all experiments. The quantitative disagreement was explained by the deficiency of the mechanism used, which treated the primary nonradical products of isoprene degradation as nonreactive. Each of these products contained a double C-C bond, which could react with radicals in solutions to influence the overall inhibiting or accelerating action. In the present mechanism, "all the work" had to be done by isoprene, which consequently appeared to

decay faster than in the experiments. The effect was more pronounced in basic and neutral solutions, because conversion of isoprene was higher than in acidic solutions. In addition, the mechanism would probably gain still more quantitaive flexibility, if included all primary nonradical products of isoprene transformation (Sect. 3.2), not the four necessary representatives (Sect. 4.3).

The ratio of simulated conversions of sulphite and oxygen was 2.0 in the absence of isoprene and 1.64–1.66 in the presence of isoprene, while the ratio of simulated conversions of isoprene and sulphite ranged from 0.28 to 0.31 (Table 3). The calculated ratios agreed well with those determined experimentally (Table 1). In the absence of isoprene all sulphite and bisulphite ions were converted into sulphate ions. Simulation showed that isoprene reduced this conversion by about 30%, as part of S^{IV} species became the substituent groups in produced esters.

$$SO_4^{\bullet -} + C_5H_8$$

$$\downarrow k_{s1}$$

$$^-O_3SOCH_2C(CH_3)=CHC^{\bullet}H_2$$

$$\big|$$

$$+ O_2$$

$$k_{s2} \downarrow$$

$$^-O_3SOCH_2C(CH_3)=CHCH_2OO^{\bullet}$$

$$SO_3^{2-} + \qquad\qquad + HSO_3^-$$

$$k_{s3b} \downarrow \qquad\qquad k_{s3a} \downarrow$$

$$^-O_3SOCH_2C(CH_3)=CHCH_2O^{\bullet} + SO_4^{2-}\ldots + H^+$$

$$SO_3^{2-} + \qquad\qquad + HSO_3^- \qquad + O_2$$

$$k_{s4b} \downarrow \qquad\qquad k_{s4a} \downarrow \qquad k_{s5} \downarrow$$

$$^-O_3SOCH_2C(CH_3)=CHCH_2O^- + SO_3^{\bullet -}\ldots + H^+$$

$$^-O_3SOCH_2C(CH_3)=CHCHO + HO_2^{\bullet}$$

$$\big|$$

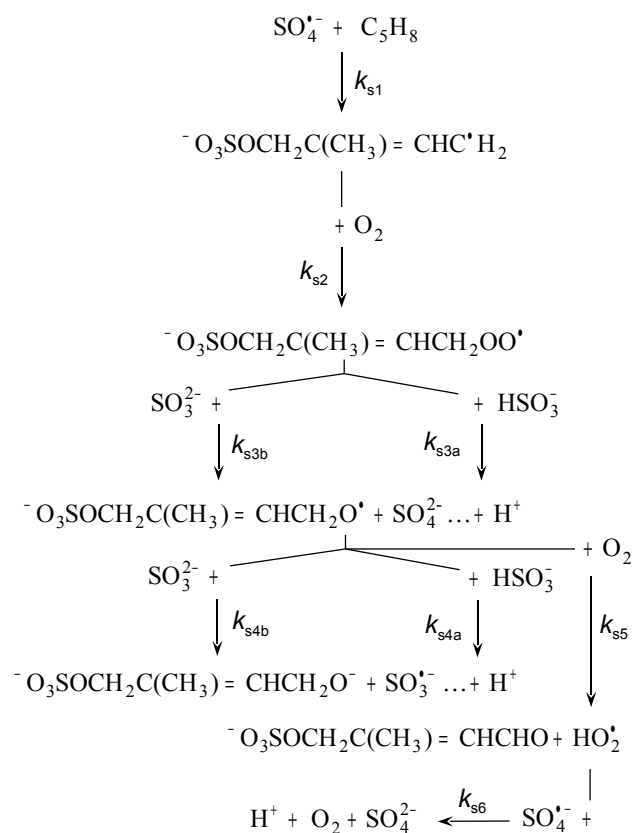$$H^+ + O_2 + SO_4^{2-} \xleftarrow{k_{s6}} SO_4^{\bullet -} +$$

Fig. 9. Mechanism of transformation of isoprene initiated by sulphate radical-anions. Similar scheme (not shown) was used for transformation initiated by sulphite radicals, with reaction constants named $k_{2s1}, k_{2s2}, k_{2s3a}, k_{2s3b}, k_{2s4a}, k_{2s4b}, k_{2s5}$, respectively.

Table 3. Model conversion ratios in transformation of isoprene coupled with auto-oxidation of S^{IV}.

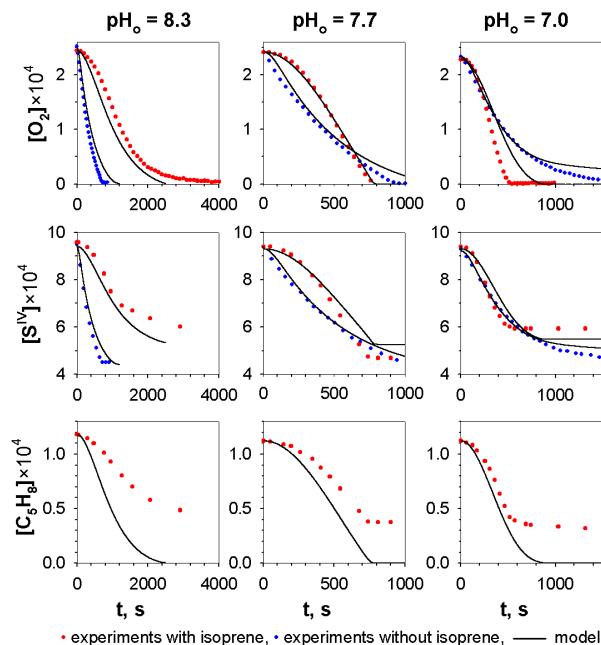| Initial pH	$\Delta\left[S^{IV}\right]/\Delta\left[O_2\right]$	$\Delta\left[C_5H_8\right]/\Delta\left[S^{IV}\right]$
8.3	1.65	0.29
7.7	1.65	0.28
7.0	1.65	0.30
5.8	1.65	0.31
4.0	1.64	0.31

Fig. 10. Chemical-kinetic simulation of temporal concentration profiles for experiments starting in basic and neutral solutions (pH$_o \geq 7$).

The acidity of reacting mixtures was reproduced quite well, with the exception of experiments that started at pH$_o$=8.3 and included isoprene, in which the experimental acidity decreased, while the simulated acidity slightly increased. This disagreement could be explained by the ability of functional groups in isoprene derivatives to bind free protons from solutions, which had not been included in the present mechanism. In acidic and basic solutions, the effect was masked by high yields of free protons released upon oxidation of HSO_3^- ions to SO_4^{2-}. It became visible in basic solutions, just because the initial reservoir of dissociable protons was smaller by orders of magnitude, while the extremely low initial concentration of free protons ($\sim 5\times 10^{-9}$ M) was very sensitive to even small shifts in the protonation-deprotonation balance of species whose concentration was higher by three or four orders of magnitude. Thus, the prediction of hydrogen ion concentration in basic solutions should improve, if the protonation and deprotonation reactions of isoprene esters are added to the mechanism.

In summary, the results of simulation showed that the proposed mechanism of isoprene transformation during autoxidation of S^{IV} was a reasonable approximation of the real-life chemistry in our experiments. The experimental and simulated data agreed very well qualitatively, and well quantitatively. The shapes of the concentration time traces, and the stoichiometry of transformation were reproduced accurately. The qualitative performance of the mechanism reflected its adequate structure. The quantitative performance can still improve within this structure, for instance if a better set of reaction rate constants is used. The working set of rate constants used for the presented simulation contained many constants, whose values were guessed by fitting, and should be replaced by values determined in future experiments. Further improvement is expected, if the mechanism is extended
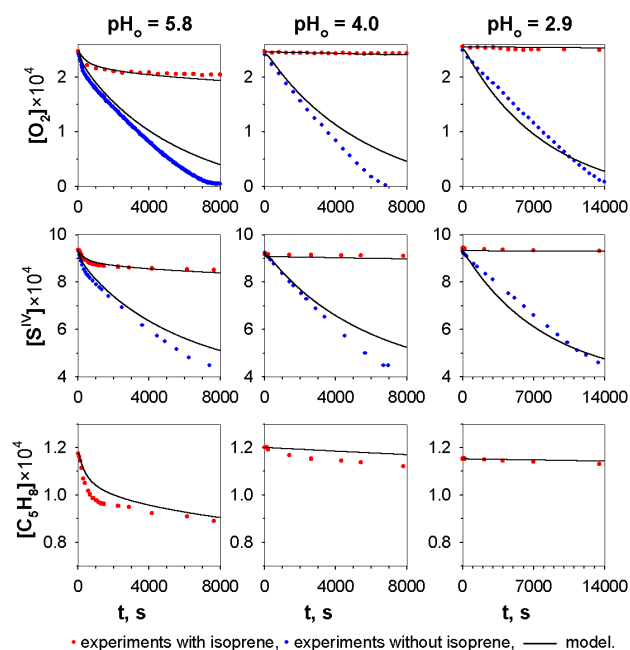
Fig. 11. Chemical-kinetic simulation of temporal concentration profiles for experiments in acidic solutions ($pH_o < 7$).

Fig. 12. Chemical simulation of temporal pH profiles for experiments at all aciditiies.

by adding the reactions indicated in this section. Despite the present limitations, the mechanism is ready for application in future studies.

5　Conclusions

We showed, by kinetic experiments, product analysis and chemical-kinetic modelling, that isoprene was capable of reacting with radicals in aqueous solutions, and turning itself into reactive radicals. Subtly regulating the balance of sulphoxy radical-anions, isoprene influenced the auto-oxidation of S^{IV} catalysed by manganese. The auto-oxidation was significantly slowed down in basic and acidic solutions, and slightly accelerated in neutral solutions. However, production of sulphate ions and build-up of solution acidity were reduced in all cases. Products of isoprene transformation included unsaturated sulphite and sulphate esters – sulphurous acid mono-(2-methyl-4-oxo-but-2-enyl) ester, sulphurous acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester, sulphuric acid mono-(2-methyl-4-oxo-but-2-enyl) ester, sulphuric acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester, and their possible structural isomers. These esters are likely precursors of saturated organosulphur compounds similar to organosulphates detected in aerosol samples from field campaigns and from simulation chamber experiments.

Reactions of isoprene with sulphoxy radical-anions have a few potential implications for atmospheric chemistry and atmosph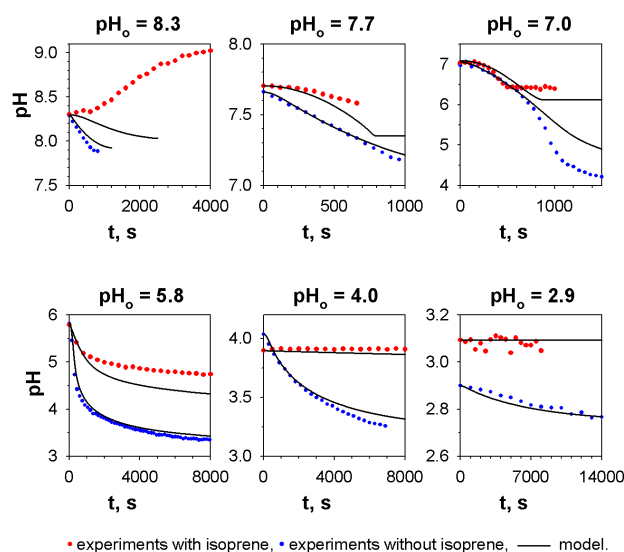ere-biosphere interactions. They are another possible source of new organosulphur components of atmospheric aerosols and waters, which add to heterogeneous sources postulated recently. They can also slow down the formation of sulphuric acid and sulphate ions in atmospheric waters, and consequently reduce the formation of acidity and inorganic sulphate aerosol. Probably, reactions of isoprene with sulphoxy radical-anions can also influence the distribution of reactive sulphur and oxygen species inside isoprene-emitting organisms (plants, animals and humans) and on their surfaces.

Realisation of reactions of isoprene with sulphoxy radical-anions in real atmospheric systems has to be evaluated quantitatively by further experimental and modelling study. The preferred systems are characterised by high availability of isoprene and S^{IV} species (sulphur dioxide), either emitted locally or transported from remote areas. Good examples are rainforests, urban areas with high emissions of vehicle exhausts, sea-coastal regions, sea-atmosphere interface and surfaces of isoprene-emitting plants. The laboratory work should focus on the uptake of isoprene by aqueous solutions, which is limited by low solubility of isoprene in water on one hand, but enhanced by aqueous reactions of isoprene and microphysical redistribution of reactants on the other hand. Products of reactions of isoprene with sulphoxy radical-anions should be searched for in field samples of atmospheric aerosols and waters.

Further research is carried out to better identify products of isoprene reactions with sulphoxy radical-anions, and to investigate further reactions of these products with sulphoxy radical-anions and other radicals.

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