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Isoprene, sulphony radicals and acidity

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Isoprene, sulphony radical-anions and acidity

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Abstract

Transformation of isoprene coupled with autoxidation of S^{IV} in aqueous solutions was studied experimentally and by chemical-kinetic modelling over 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 autoxidation 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 ($m/z=162.9$), sulphurous acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester ($m/z=164.9$), sulphuric acid mono-(2-methyl-4-oxo-but-2-enyl) ester ($m/z=178.9$), sulphuric acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester ($m/z=180.9$) – was indicated by mass spectroscopic analysis of post-reaction mixtures. The results of experiments were explained by changes in a subtle quantitative balance of three superimposed processes whose rates depended in different manner on the acidity of reacting solutions – the scavenging of sulphony radicals by isoprene, the formation of sulphony radicals during further reactions of isoprene radicals, and the autoxidation of S^{IV} itself. A chemical mechanism based on this idea was explored numerically to show good agreement with experimental data. Interaction of isoprene with sulphur(IV) species and oxygen can possibly result in formation of new organosulphate components of atmospheric aerosols and waters, and influence 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

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the atmosphere, for instance by oxidation of dimethylsulphide (Barnes et al., 2006). The recognised fate of SO₂ 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, NO₃) and by ozone, to several primary and many secondary products, such as methacrolein and methylvinyl ketone or methylglyoxal and organic nitrates, respectively (LeBras and the LACTOZ Steering Group, 1997; Fan and Zhang, 2004; Paulot et al., 2008; Taraborrelli et al., 2008).

The discovery of tetraols in ambient aerosol samples collected in Amazon rainforest and boreal K-Pusztta 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 a nutshell, numerous experiments in simulation chambers, unseeded or seeded with ammonium sulphate particles, showed isoprene induced formation of aerosol that contained such compounds as methyltetraols, C₅ alkene triols, 2-methylglyceric acid, glyoxal, methylglyoxal, acetals and hemiacetals, oragnosulphates and organonitrates, as well as oligomers of some of these. Yield and composition of aerosol depended on the presence of NO_x or SO₂ in the gas phase, or H₂SO₄ added to acidify the seed particles.

In particular, sulphuric acid and sulphur dioxide increased the yields of aerosol (Jang et al., 2002; Kleindienst et al., 2006; Surrat 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; Surrat et al., 2007a). However, recent experimental study showed direct esterification of alcohols was not feasible kinetically (Minerath et al., 2008). On the other hand, isoprene was shown to inhibit the aqueous-phase autoxidation of dissolved SO₂, 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 sulphy 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 autoxidation 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 homogeneously (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 $\text{Na}_2\text{S}_2\text{O}_5$ used in different proportions in order to obtain desired initial acidities of the reacting mixtures (Eqs. R1–R3). Only for the lowest initial acidity ($\text{pH}=2.9$), we additionally acidified the mixture with small amount of dilute sulphuric acid.



The variables recorded in each experimental run included pH, concentration of dissolved oxygen, temperature and high resolution UV spectra of reacting solutions. The

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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). These data were recorded 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, using an API 365 triple quadrupole mass spectrometer with electrospray ionization from Applied Biosystems.

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: C₅H₈ for synthesis grade, stabilised with 100 ppm of 4-*tert*-butylpyrocatechol, Na₂SO₃, Na₂S₂O₅ and MnSO₄ · H₂O 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.

3 Results and discussion

All experiments were carried out at $25.0 \pm 0.2^\circ\text{C}$. Initial concentrations of reactants were set to $(0.950 \pm 0.020) \times 10^{-3} \text{ mol dm}^{-3}$ (S^{IV}), $(0.250 \pm 0.030) \times 10^{-3} \text{ mol dm}^{-3}$ (O_2), $(0.117 \pm 0.050) \times 10^{-3} \text{ mol dm}^{-3}$ (C_5H_8), $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ (MnSO_4). The initial acidity of reacting solutions varied from $\text{pH}=2.9$ 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 exemplary 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 autoxidation of S^{IV}

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



Our previous work showed that isoprene slowed down the autoxidation of S^{IV} in solutions of $\text{pH} \geq 8$ (Rudziński, 2004). Here, we confirmed this observation for higher concentrations of isoprene, and extended the experiment to neutral and acidic solutions ($\text{pH}=3\text{--}8$).

We found that isoprene slowed down the autoxidation of S^{IV} in acidic and basic solutions ($\text{pH}_0 < 7$ and $\text{pH}_0 > 8$), but accelerated it in neutral solutions ($\text{pH}_0 = 7\text{--}8$). Figures 2 and 3 compare time traces of dimensionless concentration of oxygen ($x_{\text{O}_2} = [\text{O}_2]/[\text{O}_2]_0$) 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 autoxidation. In solutions of $\text{pH} < 5$, the uninhibited autoxidation was so slow itself, that

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isoprene could stop it almost completely. On the contrary, Figure 4 shows that in all experiments in neutral solutions, isoprene accelerated the autoxidation. The diverse influence of isoprene could result from subtle changes in a quantitative balance of three superimposed processes whose rates depended in different manner on the acidity of reacting solutions – the scavenging of sulphony radicals by isoprene, the formation of sulphony radicals during further transformation of isoprene, and the autoxidation 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 autoxidation of S^{IV} , the solutions got 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 autoxidation 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 inaccurate 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 broad peak at 240 nm (Fig. 5).

Mass spectra of post-reaction solutions contained peaks that could be attributed to products of isoprene transformation initiated by sulphite and sulphate radicals (Fig. 6): sulphurous acid mono-(-2-methyl-4-oxo-but-2-enyl) ester ($m/z=162.9$), sulphurous acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester ($m/z=164.9$), sulphuric acid mono-(2-methyl-4-oxo-but-2-enyl) ester ($m/z=178.9$), sulphuric acid mono-(4-hydroxy-

2-methyl-but-2-enyl) ester ($m/z=180.9$).

The discovered compounds have double 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 that had been detected in field samples of atmospheric aerosols (Gómez González et al., 2007; Surrat et al., 2007a).

4 Chemical mechanism and simulation of experiments

Autoxidation of S^{IV} catalysed by manganese was studied extensively in the context of environmental protection and atmospheric chemistry (Pasiuk-Bronikowska et al., 1992; Berglund and Elding, 1995; Brandt and van Eldik, 1995; Fronaeus et al., 1998; Grgić and Berčić, 2001; Ermakov and Purmal, 2002; Kuo et al., 2006). It is a chain reaction initiated by Mn^{III} and propagated by sulphonyl 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 autoxidation of S^{IV} consisted of three groups of reactions – autoxidation of Mn^{II} to Mn^{III} in presence of sulphite or bisulphite ions (Fig. 7), autoxidation 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 symbols of rate constants rather than by numbers. Values of rate constants used in simulations were collected in Table 2, along with available references.

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4.1 Group 1 – autoxidation 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 Berčić, 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}, H₂O₂ 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 oxidation 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_{dzb}) and intramolecular oxidation of second Mn^{III}, and finally decomposition of the dimer to H₂O₂ and Mn³⁺ (k_{o2a}/k_{o2b}). Unoxidised sulphite ions were released from the dimer, while oxygen molecule was used to build H₂O₂, 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 SO₃²⁻ ions and the other - with HSO₃⁻ ions, the two bound by a reversible association-dissociation reaction (k_{ass}/k_{dys}).

The extent of Mn^{III} autoxidation was very minor, and its purpose was to start the autoxidation of S^{IV} by supplying the very initial amount of Mn³⁺ in the absence of any other initiator. When the autoxidation chain grew longer, Mn^{II} was oxidised back to Mn^{III} in several reactions with sulphonyl radicals and ions. This is exactly why manganese is also called a catalyst of autoxidation.

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

Chain autoxidation of S^{IV} was initiated by formation of sulphite radical-anions in reaction of Mn³⁺ 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 SO₅²⁻ were reversibly protonated to HSO₅⁻ ions (k_{cas}/k_{cdy}). Sulphate ions were also produced in reaction of peroxymonosulphate ions with sulphite ions (k_{fa} and k_{fcb}), 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, Mn³⁺, was regenerated in reactions of Mn²⁺ 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 sulphy 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 sulphy radical. 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}). The alkyl radicals were formed that accepted oxygen molecules

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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 respective reaction 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 $-\text{OSO}_2$ substituent groups instead of $-\text{OSO}_3$.

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.

The results of simulation were compared to matching experiments in figures arranged according to 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. This observation was explained by a deficiency of the chemical mechanism used, which treated the primary nonradical products of isoprene degradation as non-reactive. Each of these products contained a double bond, which could react with rad-

icals in solution to influence the overall inhibiting or accelerating action. In the present mechanism, 'all the work' had to be done by isoprene, which appeared to decay faster.

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.

The acidity of reacting mixtures was reproduced quite well, with the exception of experiments that started at $pH_o=8.3$, in which the experimental acidity decreased, while the simulated acidity slightly increased. This disagreement could be explained by ability of functional groups in isoprene derivatives to bind free protons from solutions.

Generally, the fairly good agreement of simulated and experimental data shows that the proposed mechanism of isoprene degradation during autoxidation of S^{IV} is a reasonable approximation of the real-life chemistry. However, the rate constants used for simulation should be considered a working-set only, and not a set of determined values.

5 Conclusions

We showed, by kinetic experiment, 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 sulphony radical-anions, isoprene influenced the autoxidation of S^{IV} catalysed by manganese. The autoxidation 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-

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(2-methyl-4-oxo-but-2-enyl) ester, sulphuric acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester. These esters are likely precursors of saturated organosulphur compounds similar to organosulphates detected in aerosol samples from field campaigns and from simulation chamber experiments.

5 Reactions of isoprene with sulphonyl radical-anions have a few potential implications for atmospheric chemistry and atmosphere-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 influence distribution of S^{IV} (SO_2) and S^{VI} compounds, and reduce formation of atmospheric acidity (sulphuric acid) over isoprene-emitting ecosystems. Probably, reactions of isoprene with sulphonyl radical-anions can also influence distribution of reactive sulphur and oxygen species inside isoprene-emitting organisms (plants, animals and humans) and on their surfaces.

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

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Table 1. Experimental conversion ratios in transformation of isoprene coupled with autoxidation of S^{IV}.

Initial pH	$\Delta[\text{S}^{\text{IV}}]/\Delta[\text{O}_2]$	$\Delta[\text{C}_5\text{H}_8]/\Delta[\text{S}^{\text{IV}}]$
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 are inaccurate, because conversion of each reactant was lower than 1%.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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

Constant	Value M ⁻¹ s ⁻¹	Constant	Value M ⁻¹ s ⁻¹	Constant	Value M ⁻¹ s ⁻¹
k_{kfb}	6×10^6	k_{ib}	1.0×10^3	k_{t1}^h	4.0×10^8
k_{kbb}	1	k_{ia}	3.0×10^1	k_{t21}^i	1.0×10^7
k_{kfa}	6×10^6	k_{p1}^c	1.5×10^9	k_{t3}	1.0×10^6
k_{kba}	1	k_{p21b}^d	3.25×10^6	k_{t4}^j	5.0×10^8
k_{afb}	6	k_{p22b}^d	9.75×10^6	k_{s1}^k	2.19×10^9
k_{abb}	1	k_{p21a}^d	2.5×10^4	k_{s2}	1.0×10^9
k_{afa}	8–10	k_{p22a}^d	7.5×10^4	k_{s3b}	1.0×10^9
k_{aba}	1	k_{p3b}^e	1.4×10^7	k_{s3a}	1
k_{dfb}	6	k_{p3a}^e	1.4×10^7	k_{s4b}	1.0×10^9
k_{ddb}	1	k_{ox11}	3.2×10^6	k_{s4a}	1.0×10^9
k_{dfa}	8–10	k_{ox12}	1.2×10^2	k_{s5}	$(1-5) \times 10^4$
k_{dba}	1	k_{ox2}	1.0×10^6	k_{s6}^l	3.5×10^9
k_{o2b}	6	k_{t22}^f	1.0×10^8	k_{2s1}	1.0×10^9
k_{o2a}	8–10	k_{ass}	1.0×10^{11}	k_{2s2}	1.0×10^9
k_{hpb}^a	0.19	k_{dys}^g	6.75×10^3	k_{2s3b}	5.0×10^4
k_{hpa}^b	3.4×10^7	k_{fb}	7.5×10^3	k_{2s3a}	1.0×10^6
		k_{fa}	7.5×10^3	k_{2s4b}	$(1.2-2.5) \times 10^4$
		k_{cas}^g	1.0×10^{10}	k_{2s4a}	5.0×10^4
		$k_{c dy}^g$	3.98		

^a Drexler et al. (1992). ^b M⁻² s⁻¹, rate = $k_{hpa}[\text{H}^+][\text{H}_2\text{O}_2][\text{HSO}_3^-]$, Drexler et al. (1991).

^c Huie and Neta (1984). ^d Huie and Neta (1987). ^e Averaged in CAPRAM.

^f 5.5×10^6 Herrmann et al. (1995), $\sim 2.2 \times 10^8$ Buxton et al. (1996).

^g s⁻¹. ^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).

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

Initial pH	$\Delta[S^{IV}]/\Delta[O_2]$	$\Delta[C_5H_8]/\Delta[S^{IV}]$
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

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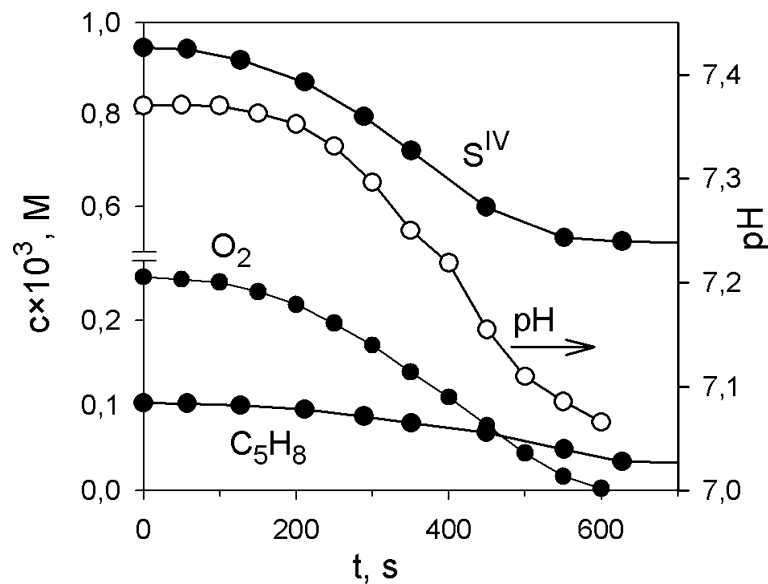


Fig. 1. Transformation of isoprene coupled with autoxidation of S^{IV} – time traces of reactant concentrations and pH obtained from an experiment in neutral solution (S^{IV} is sum of HSO_3^- and SO_3^{2-} ions).

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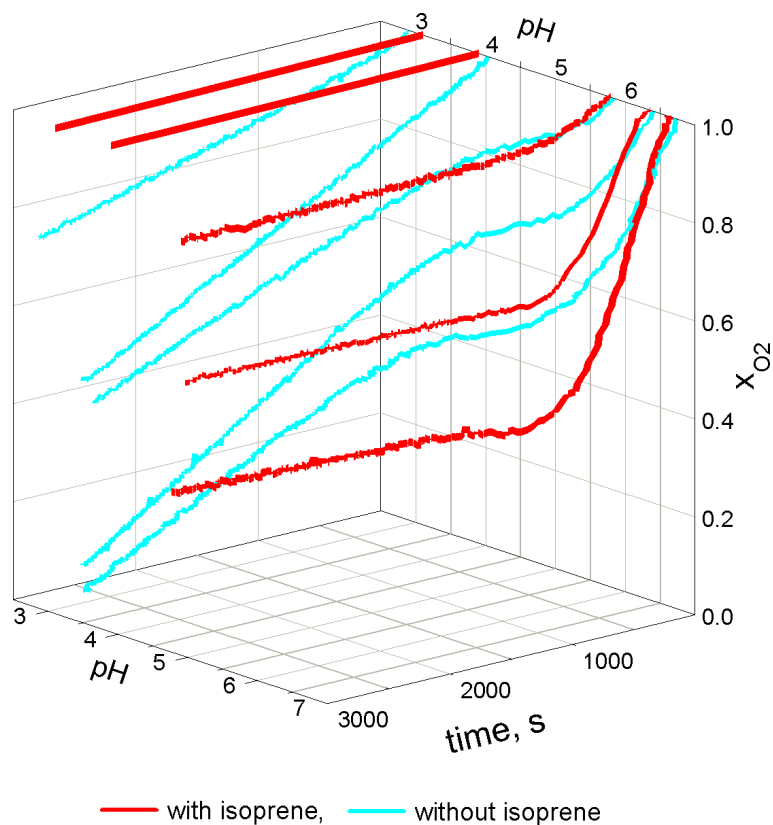


Fig. 2. Inhibition of S^{IV} autoxidation by isoprene in acidic solutions – time traces of dimensionless concentration of oxygen.

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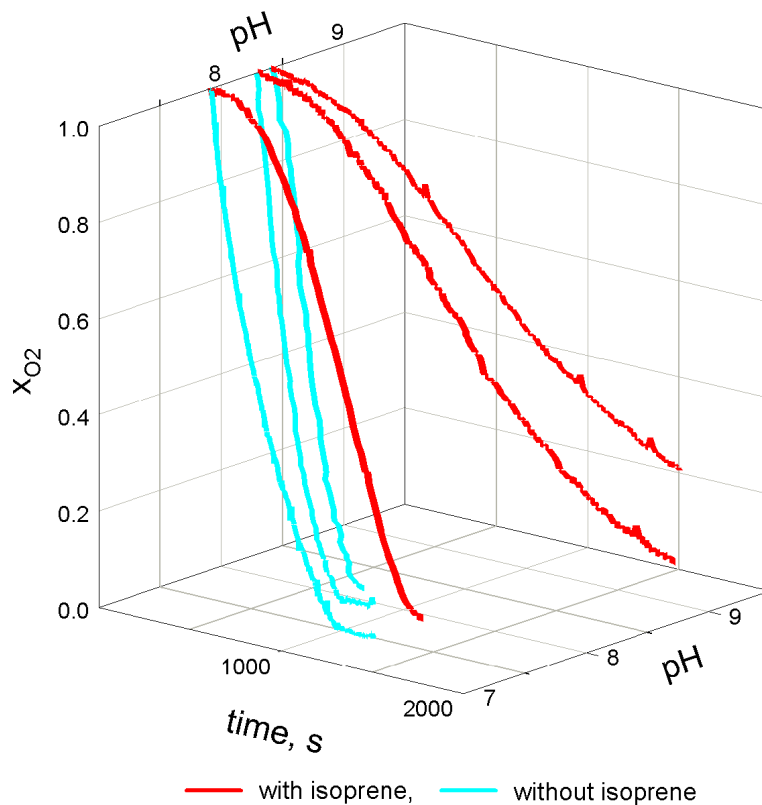


Fig. 3. Inhibition of S^{IV} autoxidation by isoprene in basic solutions – time traces of dimensionless concentration of oxygen.

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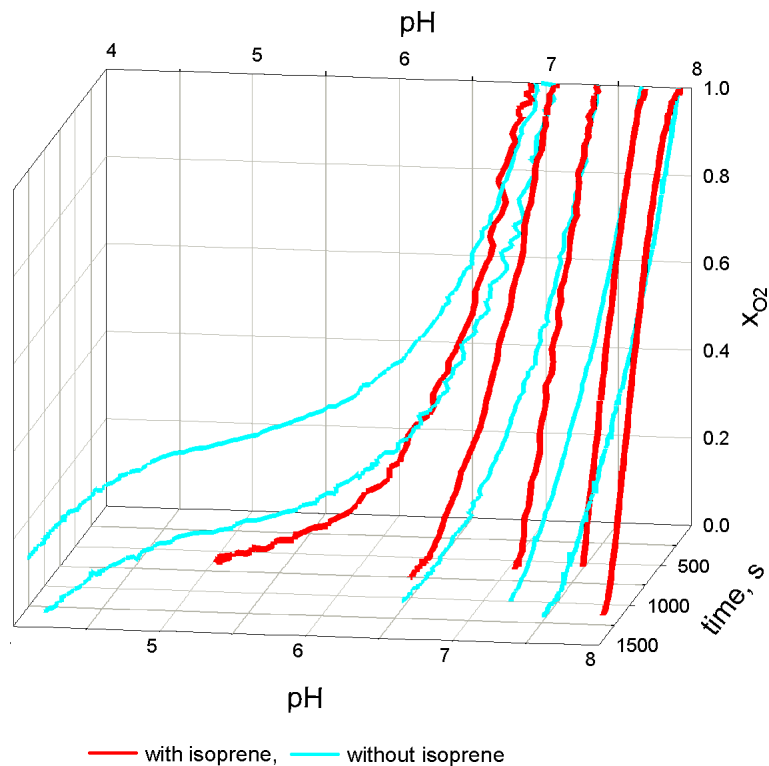


Fig. 4. Acceleration of S^{IV} autoxidation by isoprene in neutral solutions – time traces of dimensionless concentration of oxygen.

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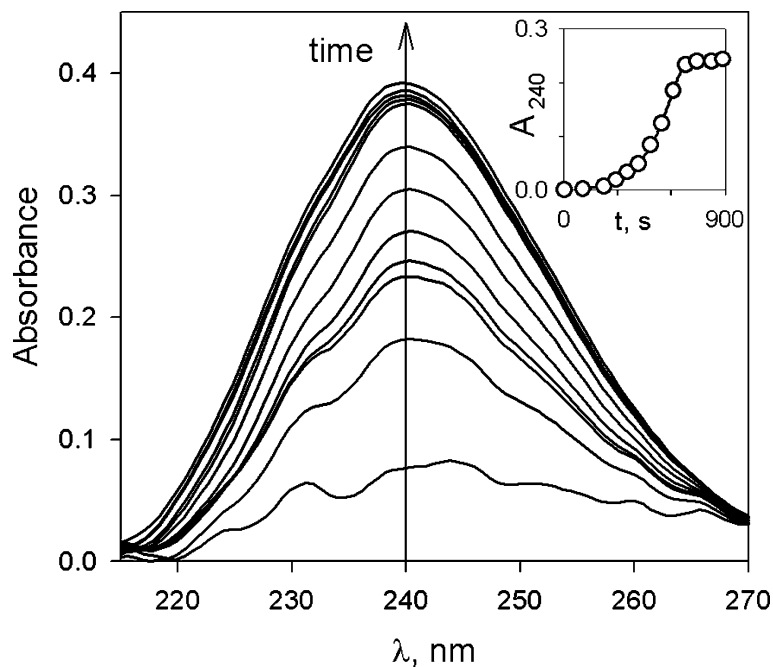


Fig. 5. UV absorption spectra of products of isoprene transformation coupled with S^{IV} autoxidation in an experiment starting at pH=6.6. Inset shows the time trace of absorbance at 240 nm.

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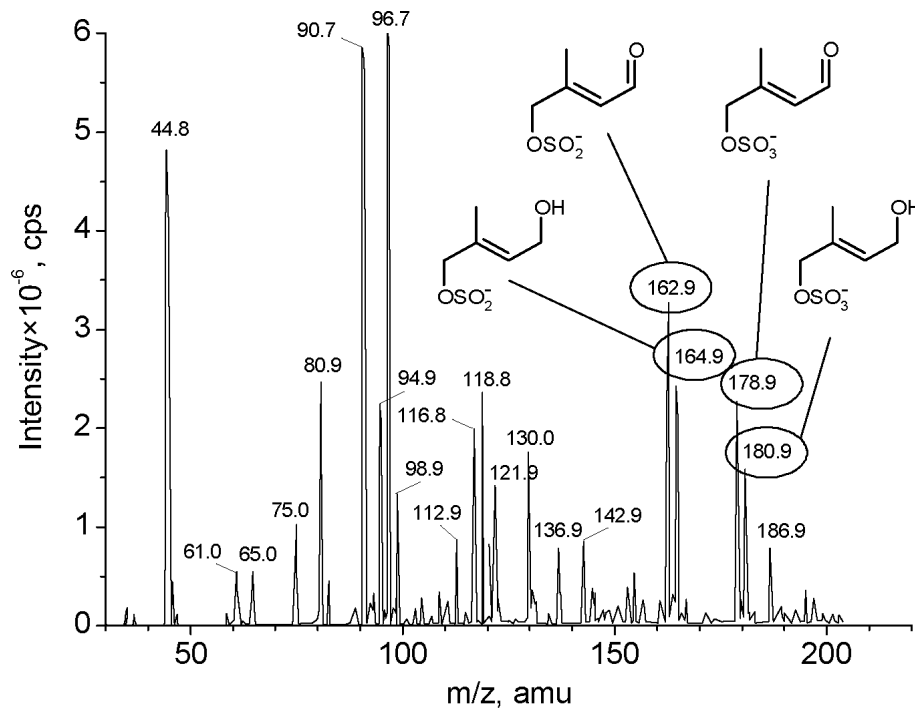


Fig. 6. Peaks corresponding to products of isoprene transformation coupled with autoxidation of S^{IV} appeared in mass spectra of post-reaction solutions.

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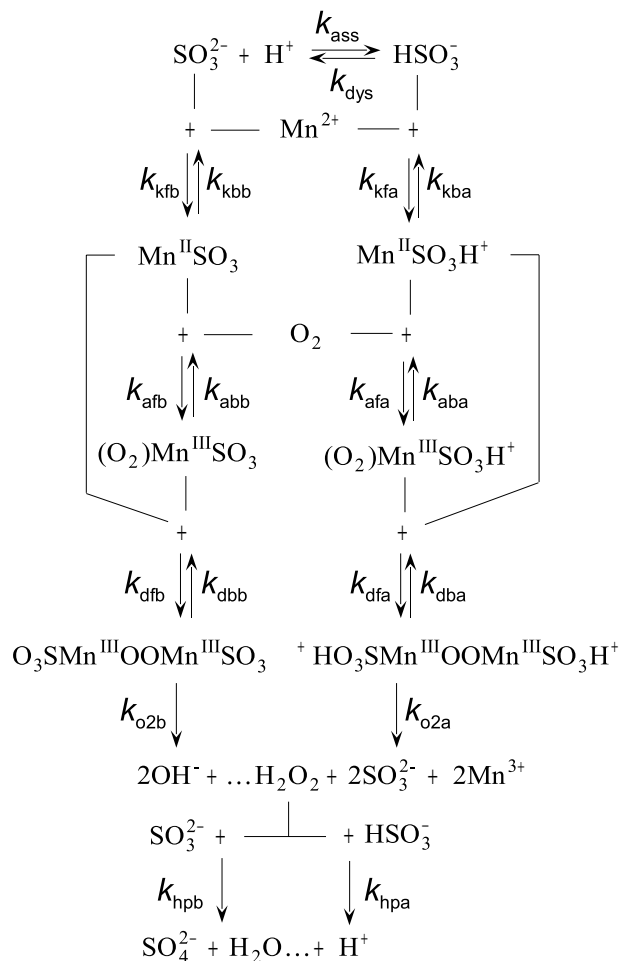


Fig. 7. Mechanism of autoxidation of Mn^{II} in the presence of sulphite and bisulphite ions.

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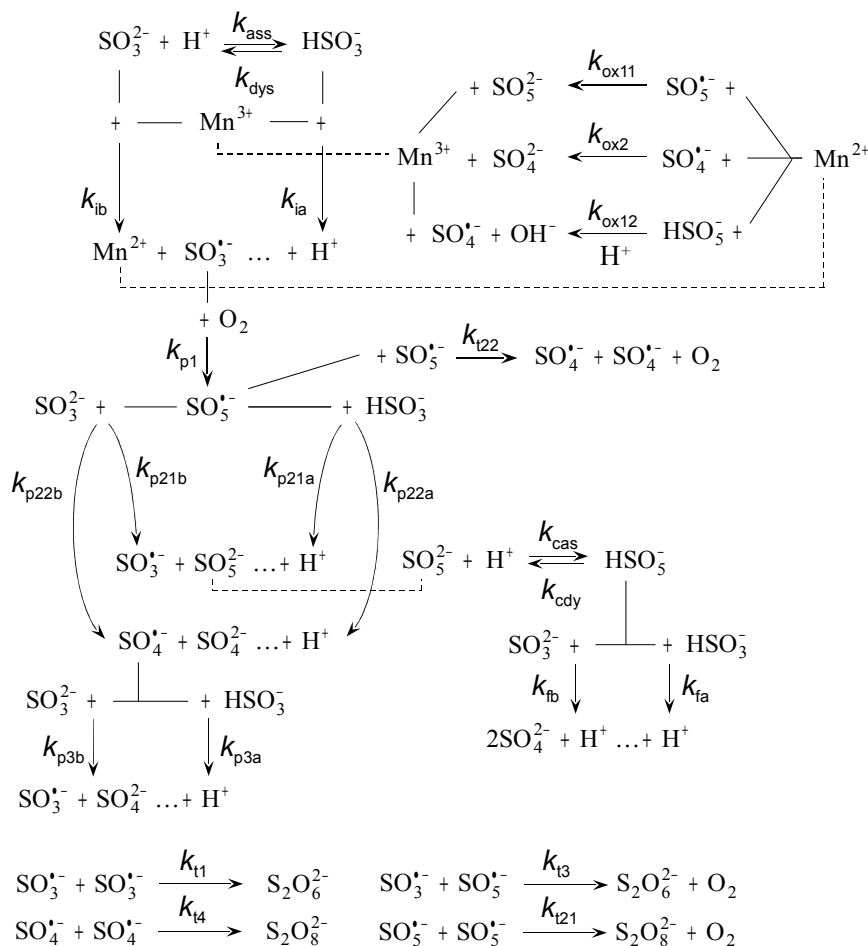



Fig. 8. Mechanism of S^{IV} autoxidation catalysed by manganese.

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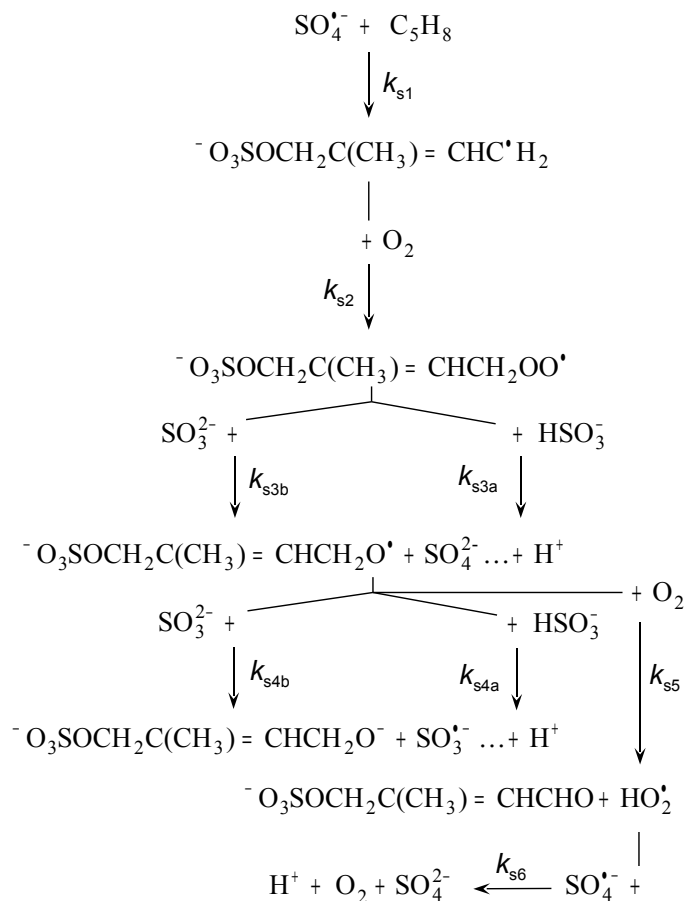



Fig. 9. Mechanism of transformation of isoprene initiated by sulphate radical-anions. Similar scheme (not shown) was used for transformation initiated by sulphite radicals, with reaction constants named k_{2s1} , k_{2s2} , k_{2s3a} , k_{2s3b} , k_{2s4a} , k_{2s4b} , k_{2s5} , respectively.

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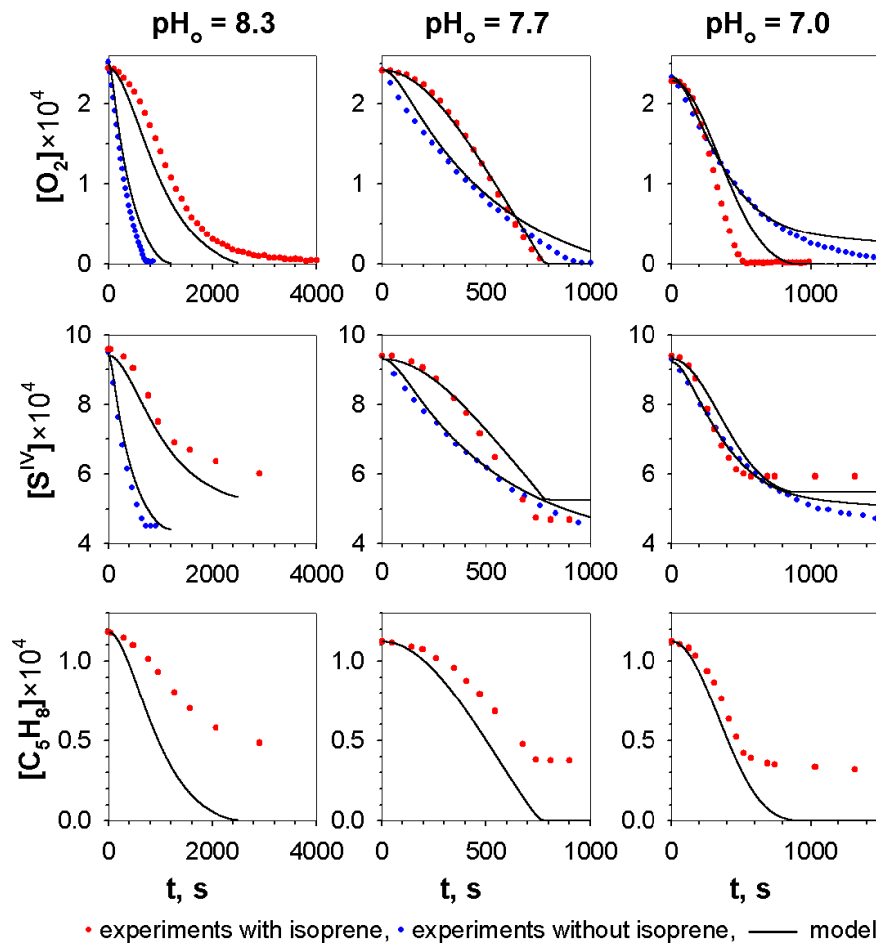


Fig. 10. Chemical-kinetic simulation of temporal concentration profiles for experiments starting in basic and neutral solutions ($\text{pH}_0 \geq 7$).

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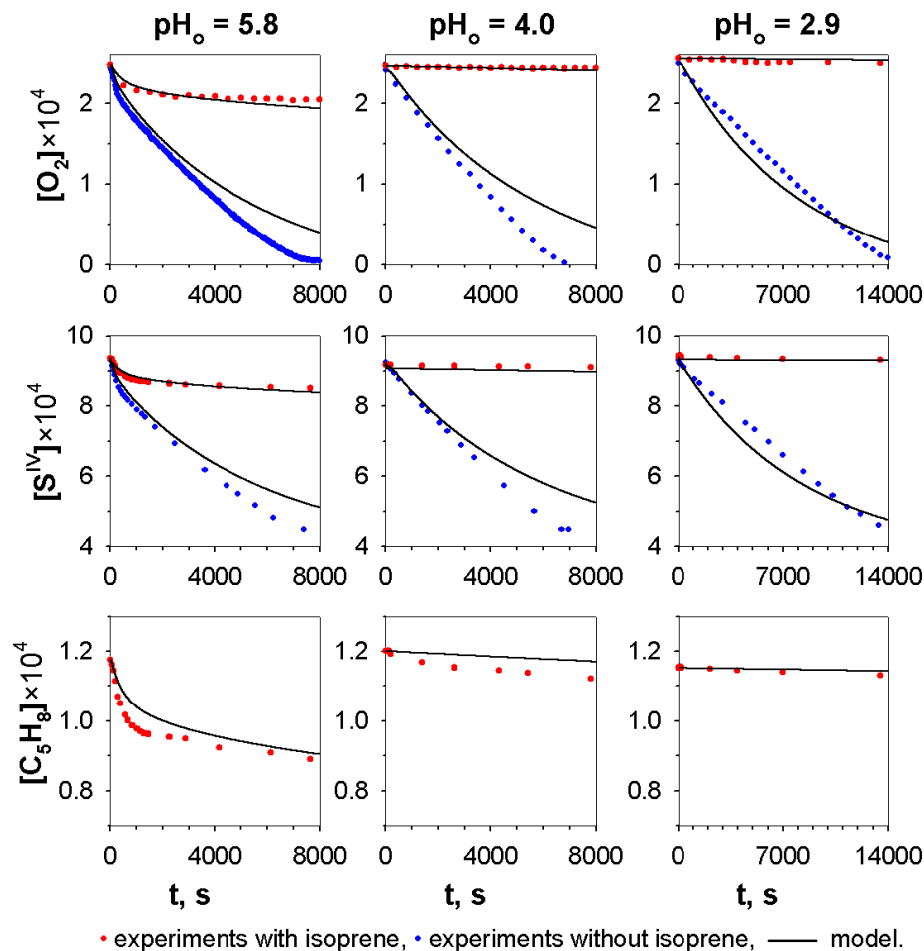


Fig. 11. Chemical-kinetic simulation of temporal concentration profiles for experiments in acidic solutions ($\text{pH}_0 < 7$).

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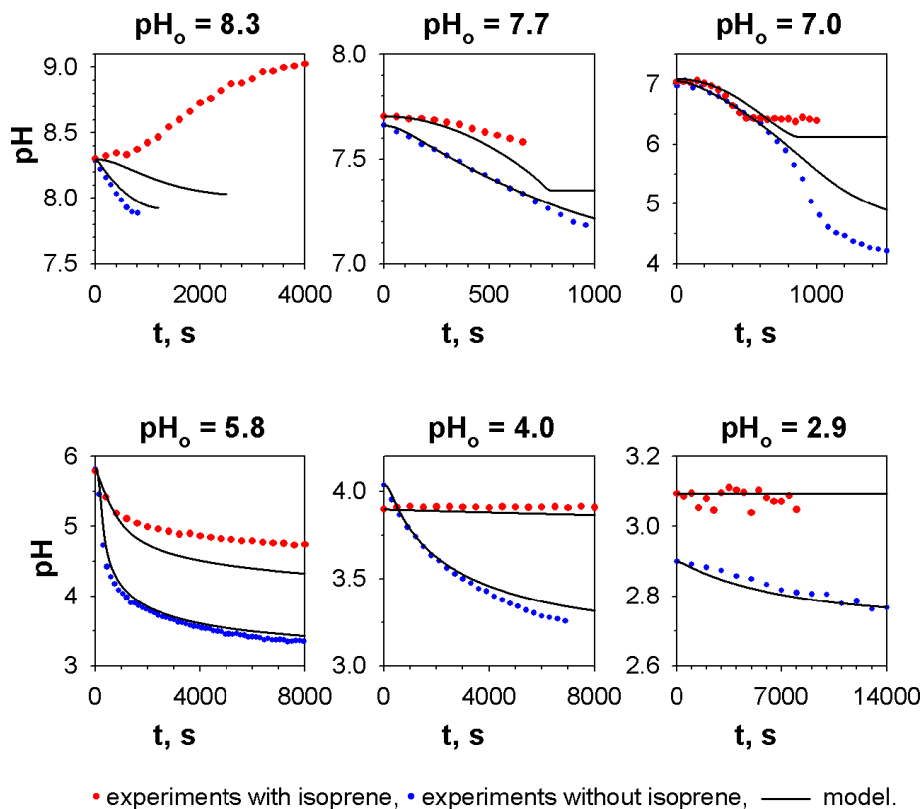


Fig. 12. Chemical simulation of temporal pH profiles for experiments at all acidities.

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