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ADDITION OF BISULFITE IONS TO METHYL VINYL KETONE AND METHACROLEIN RELEVANT TO ATMOSPHERIC PROCESSES

PRZYŁĄCZANIE ANIONÓW WODOROSIARCZYNOWYCH DO KETONU METYLOWO-WINYLOWEGO I METAKROLEINY O ZNACZENIU DLA PROCESÓW ATMOSFERYCZNYCH

Abstract: Methacrolein and methyl vinyl ketone are highly reactive carbonyls that play a pivotal role in the formation of secondary organic aerosols in the Earth's atmosphere. Both carbonyls are the major products of isoprene oxidation. We show that among the atmospheric sinks of methacrolein and methyl vinyl ketone, the aqueous-phase addition of bisulfite anions to their molecules can be relevant under polluted conditions with the increased presence of sulfur dioxide. We demonstrate that aqueous-phase reactions of methyl vinyl ketone and methacrolein with bisulfite anions lead to the formation of primary and secondary organic hydroxy-sulfonates which currently are not included in the atmospheric chemistry modelling, but can be relevant in mechanisms explaining the formation and growth of the secondary organic aerosols from atmospheric carbonyls. The rate constants for all aqueous-phase reactions involved were determined. The primary addition of bisulfite anions to methacrolein was found significantly faster than that to methyl vinyl ketone, with rate constants $k_{MAC1f} = 8$ and $k_{MVK1f} = 0.18 \ mol^{-1} \cdot dm^3 \cdot s^{-1}$ at room temperatures, respectively. The rate constant for the bisulfite addition to methacrolein was ten times faster than reported in the literature. The kinetic and mass spectrometric analyses revealed that in both cases, the dominating product was the C_4 alpha-hydroxy-sulfonate (a primary adduct), while the C_4 alpha-hydroxy disulfonate (a secondary adduct or diadduct) was produced only in trace quantities. The primary addition of bisulfite anions to methacrolein and methyl vinyl ketone should be considered in atmospheric studies relevant to areas with enhanced presence of sulfur dioxide providing sufficiently high concentrations of bisulfite ions in atmospheric waters.

Keywords: atmospheric processes, secondary organic aerosol, rate constants, electrospray mass spectrometry, LC/MS, isoprene, methacrolein, methyl vinyl ketone, sulfur dioxide, bisulfite addition, carbonyls

Introduction

Methacrolein (MAC) and methyl vinyl ketone (MVK) are primary products of isoprene oxidation in the Earth's atmosphere. The latter is the most abundant

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non-methane hydrocarbon emitted to the Earth's atmosphere [1, 2]. Methacrolein and methyl vinyl ketone are the primary products of isoprene oxidation in the gas phase. Smog chamber experiments proved that the process is driven mainly by hydroxyl radicals and to lesser extent by chlorine atoms and ozone [3–6]. Both MAC and MVK undergo further reactions in the atmosphere yielding a number of high molecular weight compounds that significantly contribute to the organic fraction of atmospheric secondary organic aerosols (SOA) [7, 8]. However, the oxidation of isoprene along with subsequent chemical processing of the products thereof is not only restricted to the gas phase but also occurs in the atmospheric waters, *eg* in cloud droplets, by means of hydroxyl and other radicals (*eg*, sulfate radicals) [9–14]. Recently, the once widely recognized then forgotten role of sulfoxy intermediates (*eg*, sulfate radicals) in the atmospheric oxidation of SO_2 was brought back to the first plan [15].

In addition, bisulfite ions HSO_3^- that originate from absorption of SO_2 in water and from dissolution of inorganic sulfites are known to add to carbonyl double bonds in aldehydes and vinyl ketones [16]. The reaction, commonly used in organic synthesis to separate aldehydes and ketones of a small molecular weight from reaction mixtures, was also recalled in the context of atmospheric chemistry [17] and determination of carbonyl compounds in ambient air [18]. The rate constant reported for the addition of HSO_3^- ions to methacrolein at 21 ^{o}C was $k_{MAC1f} = 0.65 \pm 0.03$ $M^{-1} \cdot s^{-1}$ [19]:

$$(1a)$$

$$(1b)$$
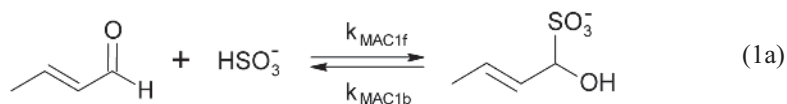
The addition of a bisulfite anion to a carbonyl double bond is reversible and leads to the formation of the C_4 alpha-hydroxysulfonate (a primary adduct). The subsequent addition of another anion to a C=C bond, which gives rise to the C_4 alpha-hydroxy-disulfonate (secondary adduct or diadduct), is irreversible and much slower. Methyl vinyl ketone is usually less reactive than methacrolein, so the addition is expected to be slower but follows exactly the same mechanism:

$$(2a)$$

$$(2b)$$
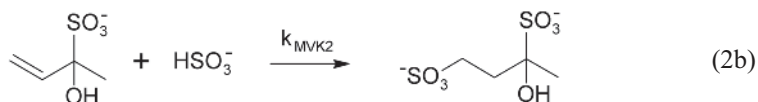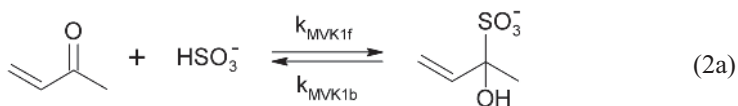
Generally, bisulfite adducts of methacrolein and methyl vinyl ketone are not included in the atmospheric chemistry modelling, however these processes are expected to be

relevant to mechanisms explaining the formation and growth of the secondary organic aerosols from atmospheric carbonyls. In our study, we decided to confirm that aqueous-phase reactions of methyl vinyl ketone and methacrolein with bisulfite anions lead to the formation of primary bisulfite adducts, using the negative mode electrospray ionization mass spectrometry hyphenated to a reversed-phase liquid chromatography. We also examined in details the kinetics and the mechanisms of the adduct formation to see if the process is relevant for the atmospheric aerosol chemistry.

Materials and methods

Chemicals

The following chemicals were used as purchased: methacrolein (Sigma-Aldrich, 95 %), methyl vinyl ketone (Sigma-Aldrich, 99 %), $Na_2S_2O_5$ (Merck, EMSURE® ACS, Reag. Ph Eur. > 98 %), acetonitrile (Sigma-Aldrich, ChromaSolv, LC/MS grade), glacial acetic acid (Roth, analytical grade) and argon (Multax 99.999 %). For each experiment aqueous solutions of reactants were prepared freshly using Milli-Q water (18.2 MΩ, Milli-Q Advantage System from Merck Millipore). To avoid the contact with the atmospheric oxygen, Milli-Q water was deoxygenated by bubbling a stream of argon over 20 min. The sodium bisulfite solutions were obtained by dissolving $Na_2S_2O_5$ in deoxygenated Milli-Q water:

$$Na_2S_2O_5 + H_2O \rightleftharpoons 2Na^+ + 2HSO_3^- \qquad (3)$$

Under the experimental conditions employed in this work, the species in solutions were predominantly Na^+ and HSO_3^- ions, while the pH of solutions was 4.

The deoxygenated Milli-Q water was also used to prepare the 0.1 % acetic acid solution, as the phase A for the liquid chromatography mass spectrometry analyses.

Measurement methodologies

The reaction of bisulfite ions with methyl vinyl ketone or with methacrolein was run in a 150 cm^3 flask reactor. The aliquots of stock solutions of reactants were mixed with water directly in the flask reactor to start the reaction. The reactor was initially filled with argon to exclude any contact of solutions with oxygen. The reacting solution was magnetically stirred and air-thermostated at 25 °C. Samples of the solution (1.5 cm^3) were drawn periodically for measurement of UV spectra. Liquid removed from the reactor was replaced with argon from the attached balloon. High resolution UV spectra were recorded in Hellma Suprasil cuvettes with a 1 cm long optical path using a Jasco V-570 spectrophotometer (200–245 nm spectral range, 0.2 nm bandwidth, 0.5 nm data pitch). Milli-Q water was used as a reference solution. Each reaction run was continued until no change in recorded spectra was observed.

Addition of bisulfite to methacrolein was also studied in a HighTech SF-61 stopped-flow spectrophotometer with a diode-array detector; because the reaction was

too fast in the initial period to be reasonably examined in the flask-reactor experiments (see the Results section). The method was suitable for reactions with a time scale of 10 ms to 100 s. Stock solutions of reactants were fed under argon atmosphere to the inlet reservoirs of the spectrophotometer, from which they were injected into the stopped-flow cell made of quartz, which had a 1 cm long optical path. Series of low resolution UV spectra of the reacting solutions were automatically recorded against the time of reaction. The spectrophotometer was calibrated daily against a holmium oxide filter at 0.794 nm bandwidth and data pitch settings. The effective spectral range used was 280–375 nm.

Table 1

Initial concentrations of reactants used in the experiments

Experiments	Methacrolein $[\text{mol} \cdot \text{dm}^{-3}]$	Methyl vinyl ketone $[\text{mol} \cdot \text{dm}^{-3}]$	HSO_3^- $[\text{mol} \cdot \text{dm}^{-3}]$
Flask reactor	$2.806 \cdot 10^{-4}$	$1.762 \cdot 10^{-4}$	$(0.84\text{–}1.02) \cdot 10^{-3}$
Stopped-flow	$3.021 \cdot 10^{-2}$		$5.026 \cdot 10^{-2}$

Calculation of concentrations

In the flask-reactor experiments, the concentrations of methyl vinyl ketone and methacrolein were determined directly from the spectra recorded, based on the fact that the absorbance of bisulfite ions was negligible at wavelengths longer than 225 nm at 25 $^{\circ}$C and on the assumption that the products of reaction (2) did not absorb light at this wavelength (Fig. 1):

$$[\text{MVK}]_{time} = A_{time}(225)/(l\varepsilon_{\text{MVK}}(225)) \tag{4}$$

$$[\text{MAC}]_{time} = A_{time}(235)/(l\varepsilon_{\text{MAC}}(235)) \tag{5}$$

where: A is absorbance at given wavelength and time, ε_{MVK} and ε_{MAC} $(\text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1})$ are the extinction coefficients of methyl vinyl ketone and methacrolein determined from the reference spectra of compounds (Fig. 2), and l (cm) is the length of the optical path.

The concentrations of bisulfite ions could not be measured directly, but were calculated from absorbances at 205 nm, assuming that the adducts produced in reactions (1) and (2) did not absorb light at this wavelength:

$$[\text{HSO}_3^-]_{time} = \frac{A_{time}(205) - [\text{MVK}]_{time}\, l\varepsilon_{\text{MVK}}(205)}{l\varepsilon_{\text{HSO}_3}(205)} \tag{6}$$

where: A are absorbances at given time and wavelength, $\varepsilon_{\text{MVK}}(205)$ and $\varepsilon_{\text{HSO}_3}(205)$ $(\text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3)$ are the extinction coefficients of methyl vinyl ketone and bisulfite ions, respectively (Fig. 4), $l = 1$ cm is the length of the optical path, and $[\text{MVK}]_{time}$ is the concentration of the ketone at given time, determined from the experiment (Fig. 6).

In the stopped-flow experiments, we used more concentrated solutions of reactants and measured the absorbances between 280 and 375 nm. The concentrations of
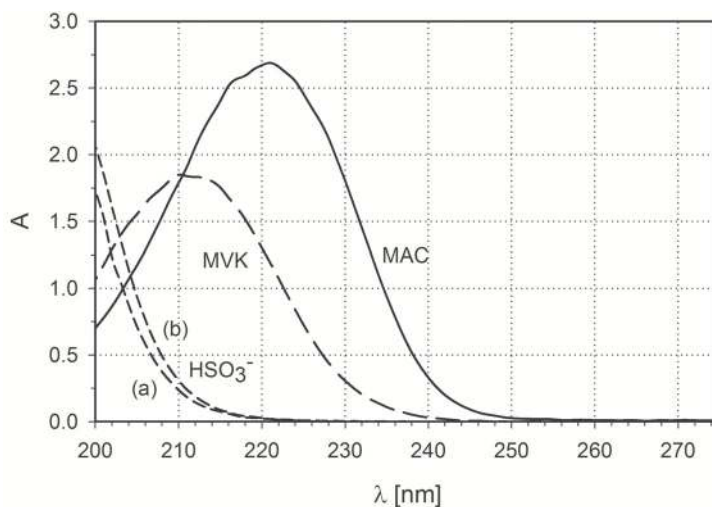
Fig. 1. UV spectra of aqueous solutions of methyl vinyl ketone ($1.762 \cdot 10^{-4}$ M), methacrolein ($2.806 \cdot 10^{-4}$ M) and $NaHSO_3$ (a – $8.498 \cdot 10^{-4}$ M; b – $1.154 \cdot 10^{-3}$ M) at 25 °C
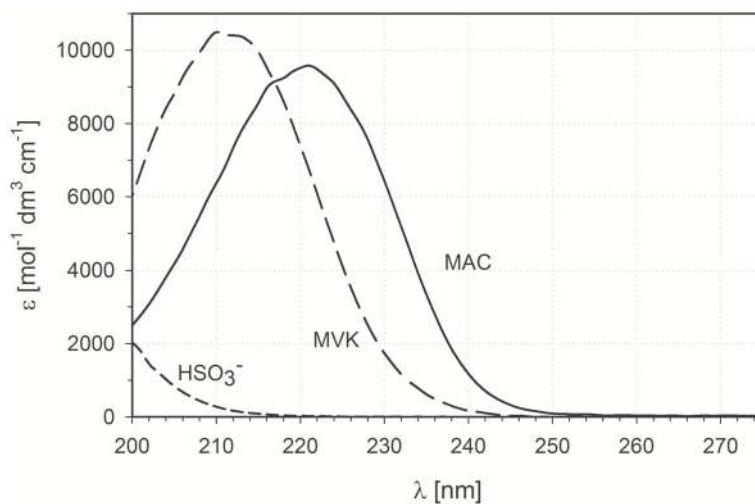

Fig. 2. Extinction coefficients of methacrolein, methyl vinyl ketone and bisulfite ions determined for the milimolar reference solutions using a Jasco V-570 spectrophotometer

methacrolein were determined directly from the spectra recorded, basing on the fact that the absorbance of bisulfite ions was negligible at wavelengths larger than 325 nm at 23 °C and on the assumption that products of reaction (1) did not absorb light at this wavelength (Fig. 3):

$$[MAC]_{time} = A_{time}(325)/(l\varepsilon_{MAC}(325)) \tag{7}$$

where: A is absorbance at given wavelength and time, ε_{MAC} (mol^{-1} · dm^3 · cm^{-1}) is the extinction coefficients of methacrolein determined from the reference spectrum (Fig. 4) and l (cm) is length of the optical path.
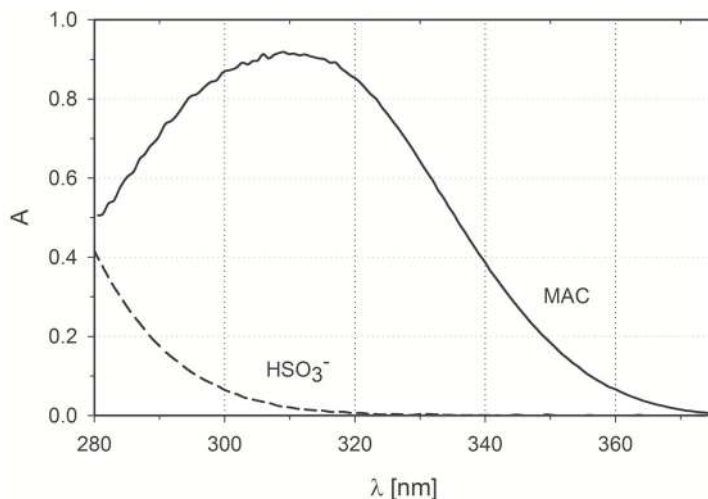

Fig. 3. UV spectra of aqueous solutions of methacrolein (3.021 · 10^{-2} M) and NaHSO$_3$ (5.260 · 10^{-2} M) at 25 ^{o}C
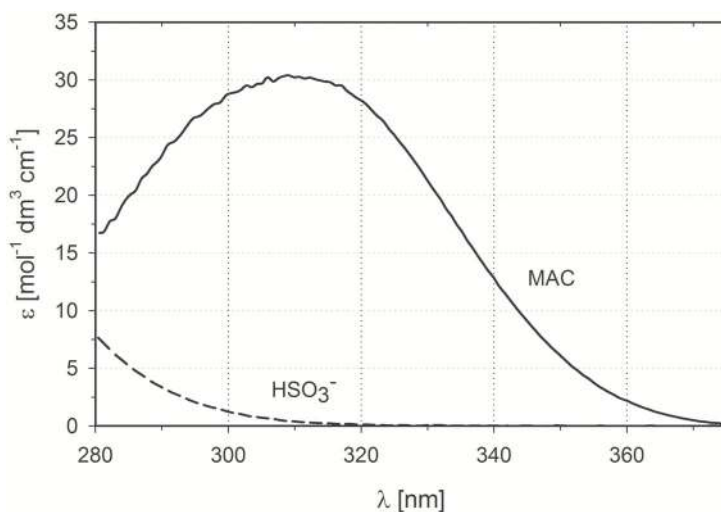

Fig. 4. Extinction coefficients of methacrolein and bisulfite ions at 25 ^{o}C determined for concentrated reference solutions using a HiTech SF-61 stopped-flow spectrophotometer

The concentrations of bisulfite ions could not be determined because calculations analogous to equation (6) produced inconsistent results probably due to very low absorbances of bisulfite ions.

Analytical methodologies

The analyses of post-reaction solutions were carried out using a high-performance liquid chromatograph (Agilent Technologies, Agilent 1100) coupled to a triple quadrupole mass spectrometer (Applied Biosystems, API 3000). The chromatographic separation was accomplished using an Atlantis T3 reversed-phase column (Waters, 100 Å, 3 μm, 2.1 mm × 150 mm) and a binary solvent system: 0.1 % acetic acid in water (phase A) – acetonitrile (phase B). The following gradient program was applied: from 0 to 5 min A – 95 %, B – 5 %, than from 5 to 10 min A – 95 % to 5 %, B – 5 % to 95 %, than from 10 to 15 min A – 5 % to 95 %, B – 95 % to 5 %, than from 15 to 20 min A – 95 %, B – 5 %. Before each injection, the aliquots of the reacting solution were diluted 100 times with the deoxygenated Milli-Q water. The flow rate of the mobile phase was kept at the level of 1 cm^3 whereas the injection volume of the sample was $10 \cdot 10^{-6}$ dm^3. The capillary voltage was set in a range of 3–5 kV. The ESI capillary was heated to 150 ^{o}C to enhance the process of the ion declustering. Nitrogen was applied as both a nebulizing and a collision gas. The mass spectrometer was equipped with an electrospray ionization source (Applied Biosystem, TurboIonSpray probe). Before each run, the collision energy was ramped and optimized for the selected ion by injecting the mixture of MAC (or MVK) and bisulfite aqueous solution using a direct injection mode. The raw data were processed using the Analyst$^®$ software (Applied Biosystems).

Results and discussion

Methyl vinyl ketone

Figure 5 shows absorption spectra recorded in a flask-reaction experiment on addition of bisulfite ions to methyl vinyl ketone. The initial spectrum (time = 0 min)
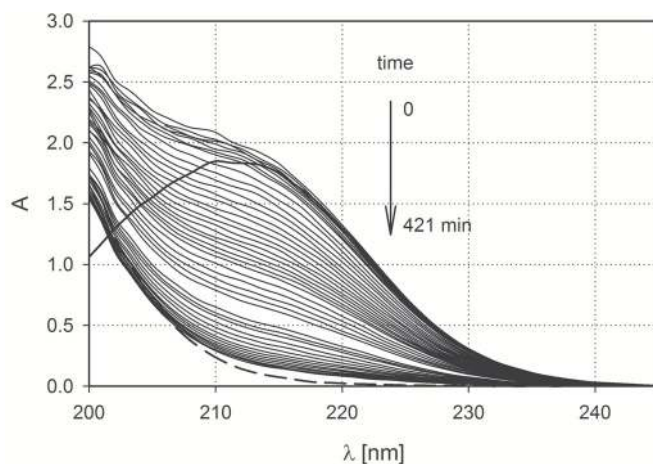

Fig. 5. UV spectra recorded during reaction of methyl vinyl ketone and bisulfite ions in aqueous solutions in a flask-reactor experiment at 25 ^{o}C, taken with a Jasco spectrophotometer. Initial concentrations of reactants were: $1.762 \cdot 10^{-4}$ mol · dm^{-3} of methyl vinyl ketone and $8.498 \cdot 10^{-4}$ mol · dm^{-3} of bisulfite (bold solid and dashed lines show respectively the spectra of individual reactants at these concentrations)

was composed from the individual spectra of aqueous solutions of methyl vinyl ketone and sodium bisulfite at concentrations equal to the initial concentrations in the reaction (bold lines in Fig. 5). With the initial concentrations of reactants at the milimolar level, the reaction proceeded fairly steadily and was completed in about 7 hours.

Figure 6 shows the time traces of substrates and reactants in the experiment. Full circles represent the experimental data while lines were obtained by solving a set of ordinary differential eequations (ODE) resulting from the chemical mechanism given in equations (2a) and (2b). Experimental time trace of methyl vinyl ketone was obtained from the cross section of absorption spectra in Fig. 5 at 225 nm. The concentrations of the ketone were calculated using equation (4) while that of bisulfite – using equation (6). Computer simulations were carried out using Mathematica$^®$ 9 software.
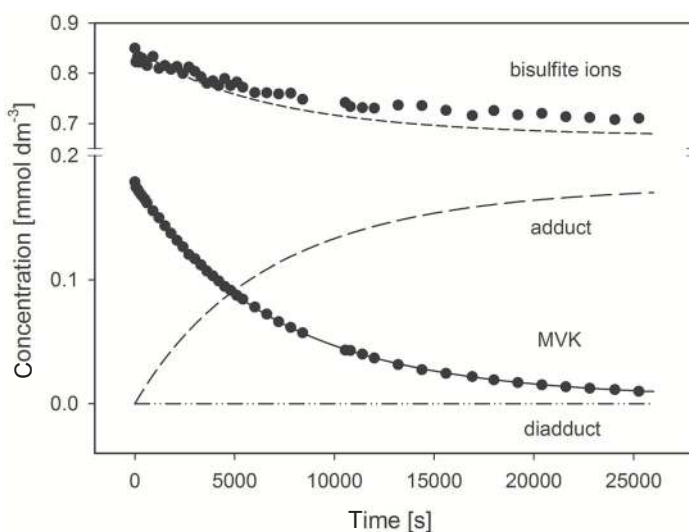

Fig. 6. Time traces of substrates and products in the reaction of methyl vinyl ketone with bisulfite ions at 25 $^{\circ}$C – experimental data (circles) from a flask-reactor experiments and computer simulation of the corresponding kinetic model (lines). Initial concentrations of reactants were: $1.762 \cdot 10^{-4}$ mol $\cdot$ dm^{-3} of methyl vinyl ketone and $8.498 \cdot 10^{-4}$ mol $\cdot$ dm^{-3} of bisulfite

Rate constants in the model were adjusted manually by the trial-and guess approach and collected in Table 2.

Table 2

Rate constants for reaction of methyl vinyl ketone with bisulfite ions in aqueous solutions at 25 $^{\circ}$C (mechanism 2a and 2b)

k_{MVK1f} [mol^{-1} $\cdot$ dm^3 $\cdot$ s^{-1}]	k_{MVK1b} [s^{-1}]	k_{MVK2} [mol^{-1} $\cdot$ dm^3 $\cdot$ s^{-1}]	$K_{MVK} = k_{MVK1f} / k_{MVK1b}$ [mol^{-1} $\cdot$ dm^3]
0.18	$3 \cdot 10^{-6}$	$1 \cdot 10^{-6}$	$6 \cdot 10^4$

Uncertainties of the constants were not evaluated because of the insuffiecient number of data.

The experimental and model data agree very well for methyl vinyl ketone and fairly well for bisulfite ions for which the deviation does not exceed 4 %. Thus, the comparison confirms the stoichiometry of reactions (2a) and (2b). The model simulation showed that the dominating product of the reactions was the ketone-bisulfite adduct, while the diadduct was produced in trace quantities, even over very long time.

The observation is in line with the results obtained from the electrospray mass spectrometry analysis of the post-reaction solution. The ESI MS/MS method was selected as the best suited technique for the direct analysis of carbonyl species from the monitored reaction in the aqueous solutions without a prior derivatization [20, 21]. While the positive ESI ion mode was used to monitor the response from methyl vinyl ketone, the reaction products were detected using negative ESI ion mode [22]. Using a direct infusion mode, the first order ESI spectrum acquired for a freshly prepared diluted mixture of MVK and bisulfite aqueous solutions showed a diagnostic peak at m/z 151 that dominate the spectrum (Fig. 7). The structure of the ion could be unambiguously assigned to the ketone-bisulfite adduct, as proved by m/z 151 $\rightarrow$ 81 transition recorded in the negative ESI product ion mass spectrum. Interestingly, the m/z 151 adduct was also observed in the ESI mass spectrum obtained for the reaction mixture separated using a reversed-phase gradient liquid chromatography. In the extracted ion chromatogram recorded at the m/z 151 channel, the corresponding peak emerged at the retention time of 4.31 min. This points to the conclusion that the MVK bisulfite adduct detected at m/z 151 is a stable product of the reaction. It is evident that its origin has nothing to do with the electrospray process in the ion source of the mass spectrometer. A careful analysis of the ESI spectrum of the post-reaction samples reveals a weak signal at m/z 116 that corresponds to a doubly charged $[M + 2HSO_3^- - 2H]^{2-}$ ion and points to the formation of the bisulfite diadduct. The signal remains weak
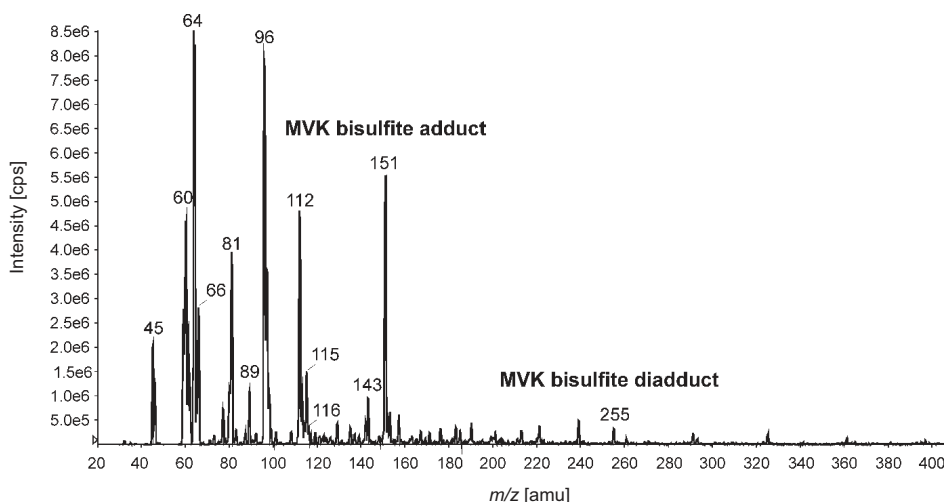

Fig. 7. First order negative electrospray mass spectrum recorded for the reaction mixture of methyl vinyl ketone and bisulfite ion taken a few minutes after mixing. The dominating signals at m/z 151 serves as a fingerprint for the formation of the MVK bisulfite adduct

even after long reaction times, indicating that the diadduct is formed in trace quantities. Another diagnostic ion for the MVK bifulfite adduct is the ion at *m/z* 255 in the form of a sodiated cluster $[M + 2HSO_3^- + Na^+]^-$.

Methacrolein

In the first attempt, the addition of bisulfite ions to methacrolein was studied in the same way as for methyl vinyl ketone, but it appeared so fast that the first spectrum that could be recorded showed already a large extent of the reaction (Fig. 8).
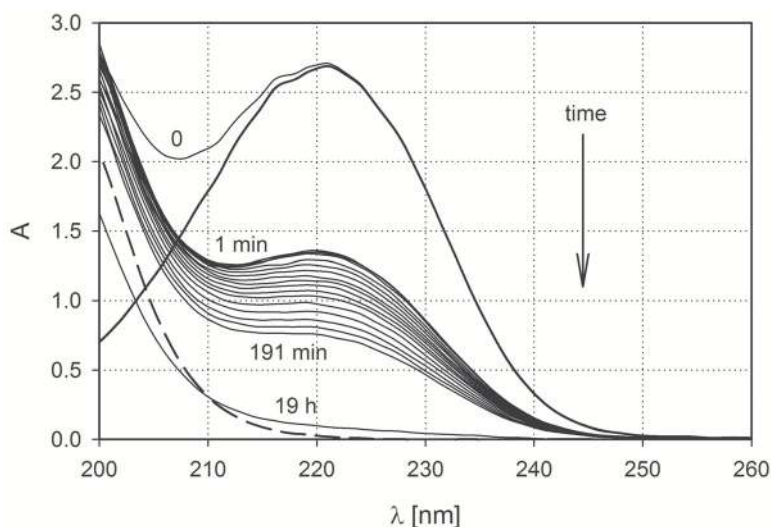

Fig. 8. UV absorption spectra recorded during the reaction of methacrolein and bisulfite ions in aqueous solution taken with a Jasco spectrophotometer in a flask-reactor experiment at 25 °C. Initial concentrations of reactants were: $2.417 \cdot 10^{-4}$ mol $\cdot$ dm^{-3} of methacrolein and $1.140 \cdot 10^{-3}$ mol $\cdot$ dm^{-3} of bisulfite (bold solid and dashed line show respectively the spectra of reactant solutions at these concentrations used to compose the spectrum of reacting solution at time 0)

To obtain complete kinetic observation, we had to use a HighTech SF-61 stopped--flow spectrophotometer with a photodiode array detector. Figure 9 shows the initial sequence of spectra recorded in a stopped-flow experiment at 23 °C. With initial concentrations of reactants at the tenfold milimolar level, the reaction proceeded initially very fast but later significantly slowed down.

Figure 10 shows the time traces of substrates and reactants in the experiment. Full circles represent the experimental data while lines were obtained by stochastic simulation of the chemical mechanism given in equation (1a) and (1b). Experimental trace of methacrolein was obtained automatically from the cross section of the absorption spectra at 325 nm. The concentrations of the aldehyde were calculated using equation (7). Stochastic simulation of the reactions was used because solutions of a corresponding ODE model with Mathematica® software inaccurately approximated
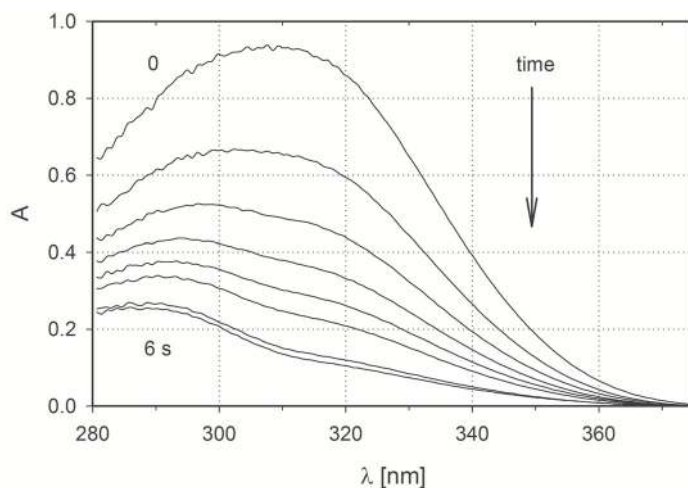
Fig. 9. A sequence of initial UV spectra recorded during reaction of methacrolein and bisulfite ions in aqueous solutions in a stopped-flow experiment at 23 ^{o}C. Initial concentrations of reactants were: $3.021 \cdot 10^{-2}$ mol $\cdot$ dm^{-3} of methacrolein and $5.260 \cdot 10^{-2}$ mol $\cdot$ dm^{-3} of bisulfite
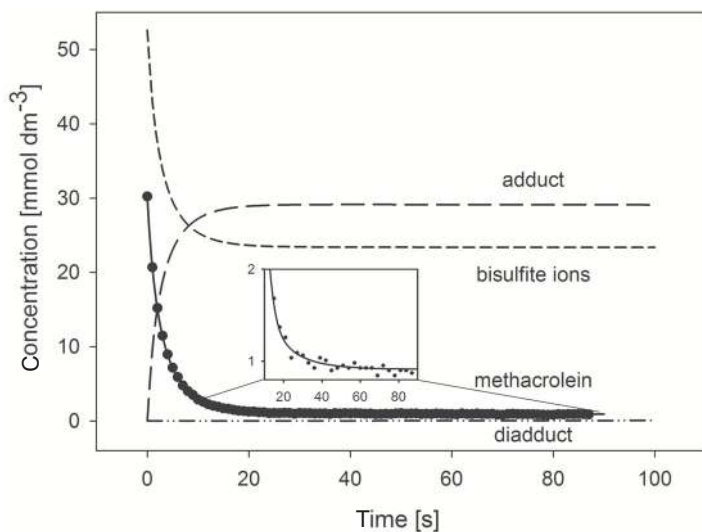

Fig. 10. Time traces of methacrolein in reaction with bisulfite ions at 23 ^{o}C – computer simulation of the kinetic model (line) compared well against the experimental data (circles) from a stopped-flow experiment. Initial concentrations of reactants were: $3.021 \cdot 10^{-2}$ mol $\cdot$ dm^{-3} of methyl vinyl ketone and $5.260 \cdot 10^{-2}$ mol $\cdot$ dm^{-3} of bisulfite

the transition from the fast period of the reaction to the slow one. The simulations were carried out using the freely available Chemical Kinetic Simulator software. Rate constants in the model were adjusted manually by the trial-and-guess approach and are collected in Table 3 along with values available from literature.

Rate constants for reaction of methacrolein with bisulfite ions in aqueous solutions
at 23 °C (mechanism 1a and 1b)

k_{MAC1f} $[mol^{-1} \cdot dm^3 \cdot s^{-1}]$	k_{MAC1b} $[s^{-1}]$	k_{MAC2} $[mol^{-1} \cdot dm^3 \cdot s^{-1}]$	$K_{MAC} = k_{MAC1f}/ k_{MAC1b}$ $[mol^{-1} \cdot dm^3]$
8 0.65*	$5.8 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	$1.38 \cdot 10^3$

* Determined at 21 °C [19]; Uncertainties of the constants were not evaluated because of the insuffiecient number of data.

The experimental and model data for methacrolein fit quite well. The reaction appeared faster by an order of magnitude than reported in the literature. The model simulation showed that the dominating product of the reactions was the methacrolein--bisulfite adduct, while the diadduct was produced in trace quantities, even over very long time.

The mass spectrometric analysis carried out for the aqueous-phase reaction of methacrolein with bisulfie ions revealed the formation of the corresponding adducts, both mono- and dihydroxysulfonates. Following the reasoning given in the paragraph on the reaction of methyl vinyl ketone with bisulfite ions, the structures of these adducts were determined based on the thorough fragmentation analysis. Using the LC/MS technique we were able to trace down the mono- and diadducts with a good base-line separation. Figure 11 shows an LC trace recorded for a sample of reaction solution with the UV detection at the 256 nm channel. The intense peak at RT 4.47 min corresponds to the MAC bisulfite adduct.

The first order negative electrospray mass spectrum recorded for the 4.47 min peak in the liquid chromatogram corresponds to the MAC bisulfite monoadduct (MW 152).
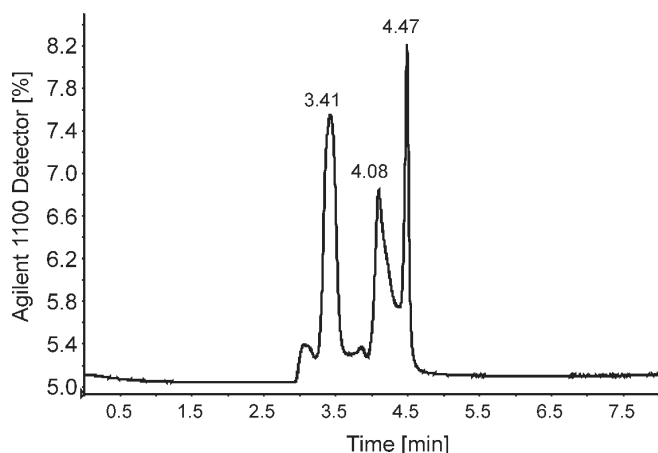

Fig. 11. Liquid chromatogram recorded for a sample from MAC reaction with the UV detection at the 256 nm channel using a tribonded C18 alkyl chain T3 column. The intense peak at RT 4.47 min corresponds to the MAC bisulfite adduct

The spectrum displays the other diagnostic ions: the $[2M - H]^-$ cluster ion at m/z 303, where M denotes the mass corresponding to the MAC bisulfite adduct in a neutral form, the $[3M - H]^-$ cluster ion at m/z 455 as well as the $[M - MAC]^-$ fragment ion at m/z 81.

Conclusions

This work presents for the first time a complete set of rate constants describing the addition of bisulfite ions to methacrolein and methyl vinyl ketone in aqueous solutions at room temperatures. The observations confirm the well-known mechanism of the reaction which consists of a reversible primary addition of bisulfite ion to a carbonyl double bond followed by a slower secondary addition of another bisulfite ion to a C=C double bond in the primary adduct. Generally, the addition to methacrolein was significantly faster than to methyl vinyl ketone. For both compounds, the dominating product was the primary adduct (C_4 alpha-hydroxysulfonate), while the secondary adduct (diadduct, C_4 alpha-hydroxydisulfonate) was produced only in trace quantities, as proved for the first time by the reverse-phase liquid chromatography electrospray tandem mass spectrometric analysis of post-reaction solutions as well as chemical kinetic modelling.

The rate constants for all reactions involved were determined by computer model-ling. The only rate constant reported in the literature for the primary addition to methacrolein was more than ten times slower than the one determined. The primary addition of bisulfite ions to methacrolein and methyl vinyl ketone should be considered in atmospheric studies relevant to areas with enhanced presence of sulfur dioxide providing sufficiently high concentrations of bisulfite ions. This regards to the conditions typical of the aerosol particle formation over forested regions with a strong anthropogenic impact.

Further research should include kinetic studies of the bisulfite additions at other temperatures, with particular attention to lower temperatures, as well as product identification studies that would confirm further the mechanism adopted in this work. Moreover, the ambient aerosol studies should include the detection of the bisulfite adducts in field samples.

Acknowledgements

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PRZYŁĄCZANIE ANIONÓW WODOROSIARCZYNOWYCH DO KETONU METYLOWO-WINYLOWEGO I METAKROLEINY O ZNACZENIU DLA PROCESÓW ATMOSFERYCZNYCH

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Abstrakt: Metakroleina oraz keton metylowo-winylowy są bardzo reaktywnymi zawiązkami karbonylowymi, które odgrywają istotną rolę w procesach atmosferycznych, w tym – w tworzeniu pyłów zwieszonych w powietrzu. Obydwa związki są produktami utleniania izoprenu – węglowodoru emitowanego do atmosfery w ogromnych ilościach. W pracy przedyskutowano mechanizmy chemiczne zaniku metakroleiny oraz ketonu metylowo-winylowego w wyniku addycji anionu wodorosiarczanowego w rozcieńczonych roztworach wodnych, odzwierciedlające procesy zachodzące w kroplach wód atmosferycznych w rejonach o znaczącym stężeniu ditlenku siarki. W pracy pokazano, że reakcje addycji anionu wodorosiarczynowego do badanych związków karbonylowych prowadzą do tworzenia pierwotnych i wtórnych hydroksysulfonianów, które mogą uczestniczyć w tworzeniu aerozoli atmosferycznych. Wyznaczono stałe szybkości wszystkich reakcji w mechanizmie addycji. Pierwotna addycja anionów wodorosiarczynowych do metakroleiny okazała się znacznie szybsza niż do ketonu metylowo-winylowego (stałe szybkości k_{MAC1f} = 8 i k_{MVK1f} = 0.18 $mol^{-1} \cdot dm^3 \cdot s^{-1}$ w temperaturach pokojowych). Stała szybkości addycji do cząsteczki metakroleiny była dziesięciokrotnie większa od stałej opublikowanej w literaturze. Analiza kinetyczna i badania produktów reakcji za pomocą spektrometrii mas wykazały, że w przypadku każdego z badanych związków karbonylowych dominującym produktem reakcji był C_4 alfa-hydroksysulfonian (addukt pierwotny), natomiast C_4 hydroksydwusulfonian (addukt wtórny, diaddukt) powstawał w ilościach śladowych. Pierwotna addycja anionów wodorosiarczynowych do metakroleiny i ketonu metylowo-winylowego może mieć znaczenie w konwersji reaktywnych związków karbonylowych w atmosferze i powinna być uwzględniana w badaniach dotyczących rejonów o znaczącej obecności ditlenku siarki, gwarantującej wysokie stężenia anionów wodorosiarczynowych w wodach atmosferycznych.

Słowa kluczowe: procesy atmosferyczne, wtórny aerosol atmosferyczny, stałe szybkości, spektrometria mas z detekcję elektrosprej, LC/MS, izopren, metakroleina, keton metylowo-winylowy, ditlenek siarki, addycja wodorosiaczynu, związki karbonylowe