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Photolysis and Heterogeneous Reaction of Coniferyl Aldehyde Adsorbed on Silica Particles with Ozone

Sopheak Net,^[a] Elena Gomez Alvarez,^[a] Natalja Balzer,^[b] Henri Wortham,^{*,[a]} Cornelius Zetzsch,^{*,[b]} and Sasho Gligorovski^[a]

The pseudo-first-order loss of coniferyl aldehyde, adsorbed on silicon dioxide particles, upon heterogeneous ozonolysis was monitored at various ozone mixing ratios in the absence and presence of simulated sunlight. For the first time we investigated the effect of light on the heterogeneous ozonolysis of coniferyl aldehyde adsorbed on silica particles. We found that UV–VIS light ($\lambda > 300$ nm) does not impact the degradation of coniferyl aldehyde by ozone but induces an additional, slow photolysis of the aldehyde with a photolytic rate constant of $\sim 10^{-5} \text{ s}^{-1}$. In both cases, that is, in presence and/or absence of light, the heterogeneous ozonation kinetics are well described by an immediate gas–surface reaction formalism with light-in-

dependent rate constants of $k_{2\text{nd}} = (7.2 \pm 0.9) \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and $(7.6 \pm 1.7) \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ in the absence and presence of light, respectively. Five oxidation products: glycolic acid, oxalic acid, vanillin, vanillic acid and 3,4-dihydroxybenzoic acid were identified and confirmed by their corresponding standards. Vanillin and vanillic acid absorb light in the region $\lambda > 300$ nm and thus can further participate in the direct and indirect photolysis processes of atmospheric relevance. A reaction mechanism is proposed in order to elucidate the ozonolysis reaction and to explain the reaction products.

1. Introduction

Wood combustion constitutes an important source of particulate matter (inorganic ash material, condensable organic compounds, and carbon-containing particles), as well as a source of a complex mixture of gases, some of them known due to their carcinogenic and mutagenic properties.^[1–4] An increase in aerosol concentration may give rise to adverse side effects, such as visibility reduction,^[5] and wood smoke particles are predominantly in the inhalable size range,^[1,3,6–7] thus increasing the possibility of adverse health effects.^[8] In addition, the carbonaceous material may contribute significantly to the global warming due to its light absorbing properties.^[9]

Natural wood is a complex and highly variable material consisting of two major chemical components, carbohydrates (40–50%) and lignin (18–35%).^[10–13] The lignin pyrolysis products, methoxyphenol and methoxybenzaldehyde, are major components in the fine particulate matter of wood smoke and are also detected in urban atmospheric samples.^[10,14] One of the major pyrolysis products of lignin is coniferyl aldehyde. Its emission rate has been determined to be 125 mg kg^{-1} of burnt wood;^[10] yet, its reactivity in the atmosphere has not been determined. The organic coated aerosol particles can be transported long-distance^[15–18] and during this travel they can interact with trace gases such as ozone. Ozone is especially effective in the oxidation of molecules containing unsaturated carbon–carbon bonds.^[19–24]

Coniferyl aldehyde contains unsaturated carbon–carbon bonds in the aromatic ring and an unsaturated alkene carbon–carbon bond which are specific sites for reaction with ozone.

At the lowest altitudes, all of the high-energy UV radiation is attenuated, leaving only light of $\lambda > 290$ nm to effect any photochemistry. The absorption cross section of coniferyl aldehyde is shifted into the tropospheric actinic window ($\lambda > 290$ nm), so direct and indirect photolysis processes may be also a factor of its aging.

Herein, kinetic measurements of the heterogeneous reactions of gas-phase ozone with coniferyl aldehyde adsorbed on silica particles in presence and absence of light were performed and the consecutive reaction products were identified using the gas chromatography mass spectrometry (GC-MS) technique.

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2. Results and Discussion

2.1. Kinetics of Heterogeneous Reactions

2.1.1. Method Validation

Coniferyl aldehyde is a semivolatile compound with a vapour pressure of 2×10^{-5} Torr.^[59] For the kinetic measurements, 15 exposures were performed to determine the loss of coniferyl aldehyde by the flow of the $N_2/O_2/O_3$ mixture. Different experimental conditions were chosen: blank without exposure, exposure to N_2 , exposure to O_2 , exposure to O_3 at 6 ppm in the dark and under simulated sunlight. Each exposure was performed with the same flow of gas (150 mL min^{-1}) and was repeated three times for an exposure time of 7 h. Figure 1 shows

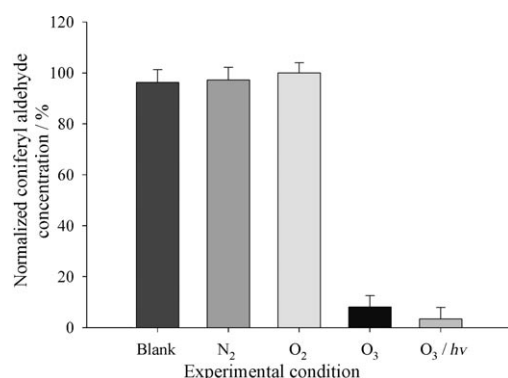


Figure 1. Normalized concentration of coniferyl aldehyde adsorbed on silica particles for five different conditions of exposure. Blank: adsorbed coniferyl aldehyde without gas exposure; N_2 , O_2 , O_3 and $O_3/h\nu$: adsorbed coniferyl aldehyde exposed to N_2 , synthetic air N_2/O_2 , $N_2/O_2/O_3$ with an ozone mixing ratio of 6 ppm under dark condition and O_3 (6 ppm) under simulated sunlight, respectively.

the normalized concentration of coniferyl aldehyde adsorbed on silicon dioxide for five different exposure conditions and the error bars obtained from the standard deviations (considering Student's *t* factor) of three repeated experiments each.

The results depicted in Figure 1 show that the gas flow used in this study did not influence the quantity of coniferyl aldehyde adsorbed on silicon dioxide in the reaction chamber. A loss of coniferyl aldehyde was observed only when the coated particles were exposed to ozone in presence and absence of light. Under dark conditions, coniferyl aldehyde did not react with O_2 (Figure 1). The concentrations of coniferyl aldehyde remained the same when particles of coniferyl aldehyde adsorbed on silicon dioxide were exposed to N_2 or O_2 compared to blanks without gas exposure. These results demonstrate that the adsorption procedure was reproducible and that volatilization was negligible under the experimental conditions used. Thus, blank exposures to N_2 were used as reference for the kinetic measurements.

2.1.2. First-Order Rate Constants

The heterogeneous reaction between ozone in the gas-phase and coniferyl aldehyde adsorbed on the surface of silica parti-

cles was investigated by monitoring the intensity of the GC-MS signals. The latter was done under dark conditions (A) and under simulated sunlight irradiation (B). In both cases, an irreversible loss of coniferyl aldehyde was observed. The loss of coniferyl aldehyde is illustrated in Figure 2 by typical profiles

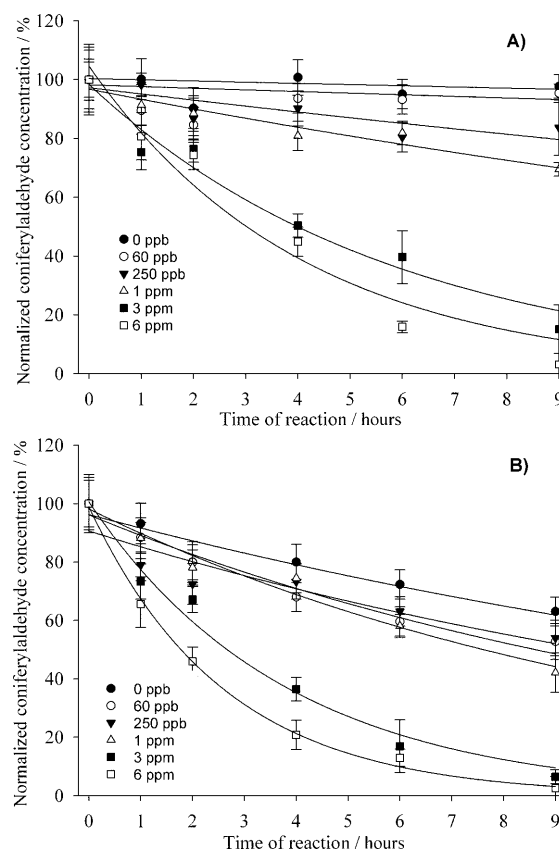


Figure 2. Decays of normalized concentrations of coniferyl aldehyde adsorbed on silicon dioxide for six different ozone concentrations. A) Ozonolysis in the dark B) Ozonolysis in presence of light.

of the normalized concentration as a function of the reaction time for various ozone concentrations with a fixed initial reactant concentration.

These normalized concentrations of coniferyl aldehyde were derived from the chromatographic peak area as $[\text{Conif}]_t/[\text{Conif}]_0$, where $[\text{Conif}]_t$ is the peak area corresponding to the concentration of coniferyl aldehyde at time *t* and $[\text{Conif}]_0$ the peak area related to the initial concentration of coniferyl aldehyde. Experimental data points were fitted using an exponential function (Equation 1), where k' is the pseudo-first-order rate constant:

$$\frac{[\text{Conif}]_t}{[\text{Conif}]_0} = \exp(-k' t) \quad (1)$$

The pseudo-first-order rate constants derived from these exponential decay curves were plotted versus the ozone concentrations (Figure 3).

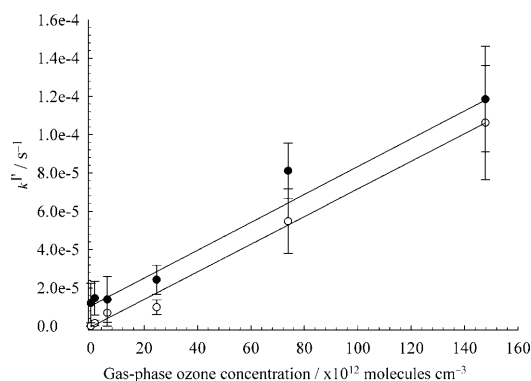


Figure 3. Observed apparent rate constant k' versus gas-phase concentration of ozone under dark conditions (○) and under simulated sunlight irradiation (●).

Both under dark conditions and with illumination of the surface, a heterogeneous elementary gas–surface reaction was observed in which ozone from the gas phase directly reacts without a separate step of surface accommodation prior to the reaction. This is in contrast to our previous studies,^[25–27] where we observed enhanced loss of the adsorbed organic compounds upon light irradiation of the surface and a change to a nonlinear Langmuir–Hinshelwood mechanism. On the other hand, it confirms our hypothesis^[25] that the rates of oxidation can be described either by linear regressions known as elementary gas–surface reactions or by a nonlinear Langmuir–Hinshelwood mechanism which in turn is strongly dependent on the nature of the surface, structure of the molecules and type of the oxidants. In both cases, in total darkness and under simulated sunlight illumination, a linear dependence is found ($R^2=0.99$ for the experiment under dark condition and $R^2=0.92$ for the experiment under simulated sunlight) (Figure 3). From the regression line plotted in Figure 3 a second-order rate constant of $k_{2nd}=(7.2\pm0.9)\times10^{-19}\text{ cm}^3\text{ molec}^{-1}\text{ s}^{-1}$ was derived for the ozonolysis experiments carried out in total darkness and $k_{2nd}=(7.6\pm1.7)\times10^{-19}\text{ cm}^3\text{ molec}^{-1}\text{ s}^{-1}$ (at 297 K) for the experiment under simulated sunlight. The intercept of the regression line is zero for the experiment under dark conditions and the regression line in the presence of light gives a photolytic rate constant of $(1.2\pm0.9)\times10^{-5}\text{ s}^{-1}$, independent of the presence of ozone. The observed photolytic rate constant implies that direct photolysis is the predominant reaction channel acting as a sink for coniferyl aldehyde in the atmospheric environment. This is not unexpected since coniferyl aldehyde in neutral media absorbs light at $\lambda>300\text{ nm}$ with a maximum at 340 nm.^[28] The UV absorption spectrum was determined in n-hexane and water and is shown in Figure 4. The absorption extends to 350 nm in n-hexane (considered as a model for the gas-phase spectrum) and to 400 nm in water which is in excellent agreement with the spectra determined by Skurikhin.^[28] The overlap with the solar spectrum above 300 nm is considerable and explains the observed photolysis. The strong bathochromic shift of the spectrum in water might be relevant for aerosol-borne coniferyl aldehyde as well.

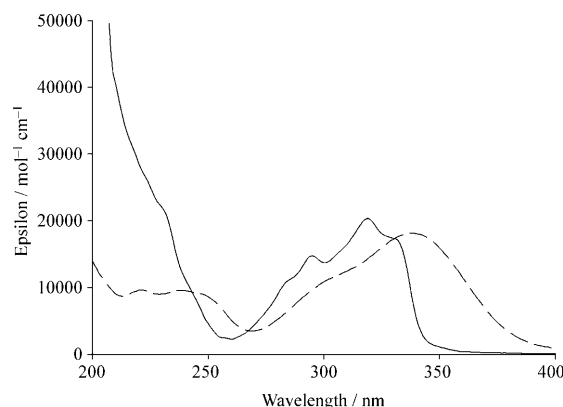


Figure 4. UV absorption spectra of coniferyl aldehyde in n-hexane [—] (3.4 mg L^{-1}) and water [----] (2 mg L^{-1}) determined by a UVIKON XL spectrophotometer in 1 cm cuvettes.

The photochemical transformation of coniferyl aldehyde occurs over a broad spectral range (300–400 nm) with an approximate overall quantum yield of about 1.4×10^{-5} at a light intensity of $150\text{--}200\text{ W m}^{-2}$ at a distance of 25 cm from the reactor and with 6 ppm of ozone and 9 h of exposure.

It was reported that the largest negative charge in the ground state is located on the oxygen atom of the carbonyl group present in the coniferyl aldehyde molecule.^[33] When the particles coated with coniferyl aldehyde are illuminated by simulated sunlight, the negative charge on the oxygen atom of the C=O group further increases when the molecule is excited from the ground state to the triplet state. The latter implies a raise of the nucleophilic properties of the molecule which is most likely responsible for the high reactivity of carbonyl compounds in their excited triplet states.

On the other hand, in the vinyl group of coniferyl aldehyde the carbon atoms do not bear big negative charges in the ground state.^[29] But again, with illumination of the particle surface, coniferyl aldehyde is passing from the ground state to the excited triplet state with a large increase of the negative charge on the carbon atoms of the vinyl group. The latter could be the reason for the enhanced degradation of coniferyl aldehyde under light irradiation of the particles' surface.

In addition to degradation of coniferyl aldehyde in presence and absence of light, the evolution of the main products (vanillin and vanillic acid, see Section 2.2.) was determined quantitatively. Figure 5 shows the differences in mass of vanillic acid and vanillin formed during ozonolysis of coniferyl aldehyde under dark conditions (Figure 5A) and under simulated sunlight illumination of the silica surface (Figure 5B).

The mass of vanillin expressed in mg was higher in the experiment under dark condition than under sunlight illumination of the surface. Typically, there is a linear increase of vanillic acid (Figure 5A,B) and of vanillin (Figure 5C,D). At the highest level of ozone exposure (6 ppm) the growth of vanillin becomes convex, indicating that vanillin undergoes further reactions. The linear regressions in Figure 5C imply a blank value of 4 mg. The shown curve is a fit of the function $f = [\text{vanillin}]_0 + a(1 - \exp(-bt))$ to the data and gives a blank

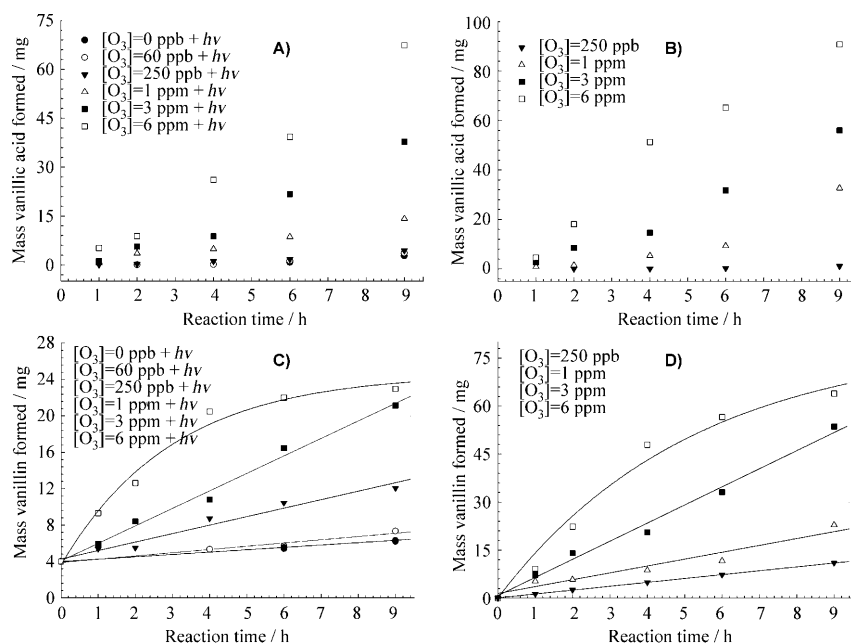


Figure 5. Vanillic acid formed during ozonolysis of coniferyl aldehyde at various ozone levels as a function of time: A) under simulated sunlight illumination of the silica surface, B) under dark conditions. Vanillin formed: C) under simulated sunlight illumination and D) under dark conditions.

value of $[\text{vanillin}]_0 = 3.6$ mg (in agreement with the intercept of the regression lines), a rise rate of $b = 0.33 \text{ h}^{-1}$ and a maximum yield of $a = 21$ mg. In Figure 5D the regression lines pass through zero and again the data at 6 ppm of ozone can be described by a function $f = a(1 - \exp(-bt))$ with $a = 80$ mg and $b = 0.19 \text{ h}^{-1}$. These functions are merely a guide to the eyes and do not have any mechanistic relevance.

The evolution of other reaction products are not presented because they were very low, often very close to the detection limit.

2.2. Identification of the Oxidation Products

The reaction samples were analyzed by GC-MS in two ways: directly and after derivatization with bis(trimethylsilyl)-trifluoroacetamide (BSTFA). Figure 6 shows the chromatograms of coniferyl aldehyde taken before and after 7 h of exposure to ozone (mixing ratio of 6 ppm). All the compounds are well-separated and exhibit well defined peaks. Two peaks (numbered 1a and 2b in Figure 6A) of the reaction products were detected in the chromatogram obtained by direct analysis (Figure 6A). After the derivatization with BSTFA, more peaks were detected (Figure 6B) and can be compared with the chromatogram depicted in Figure 6A. The chromatogram (Figure 6B) obtained with BSTFA derivatization allows identification of organic compounds which contain $-\text{OH}$ and/or $-\text{COOH}$ moieties. These groups cannot be detected by direct analysis because of the strong interaction with the stationary phase in the chromatographic column or due to the small amount of products formed during the reaction.

A first, preliminary identification of the reaction products was carried out based on characteristic fragments and by com-

paring each product mass spectrum to a library mass spectrum.^[60] Identified products were then confirmed by double standard analysis (directly and after derivatization with BSTFA). Five oxidation products (glycolic acid, oxalic acid, vanillin, vanillic acid and 3,4-dihydroxybenzoic acid) were identified and confirmed by the authentic standards. Four peaks (6b, 7b, 8b and 10b, depicted in Figure 6B) were recognized as vanillin. An analysis of a vanillin standard compound after derivatization with BSTFA shows four peaks at the same retention times as the peaks 6b, 7b, 8b and 10b, with the same characteristic ion fragments. Peak 6b corresponds to a vanillin derivative, peak 10b corresponds to an acetal artefact which is likely formed through the reaction of BSTFA with the

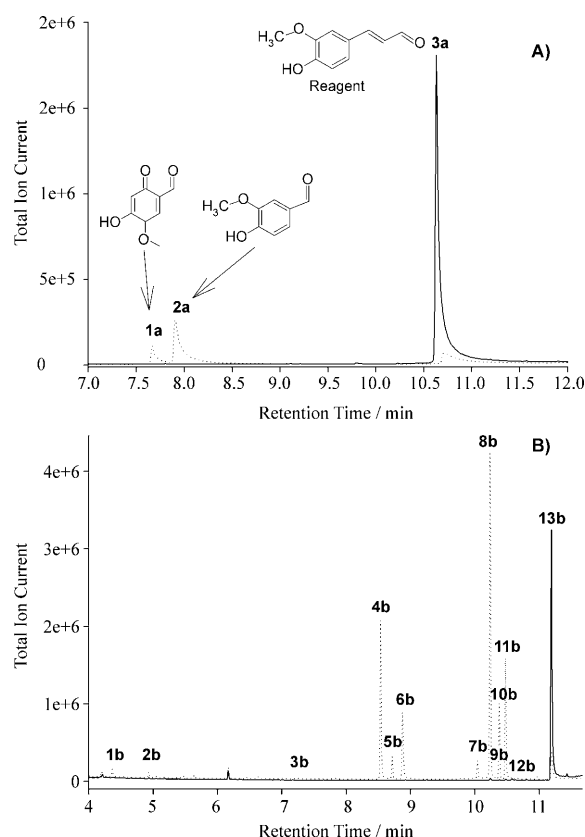


Figure 6. Total ion chromatogram taken before (—) and after 7 h (.....) of ozone exposure (6 ppm) of the particles coated with coniferyl aldehyde. A) Total ion chromatogram of direct GC-MS analysis and B) total ion chromatogram after derivatization with BSTFA.

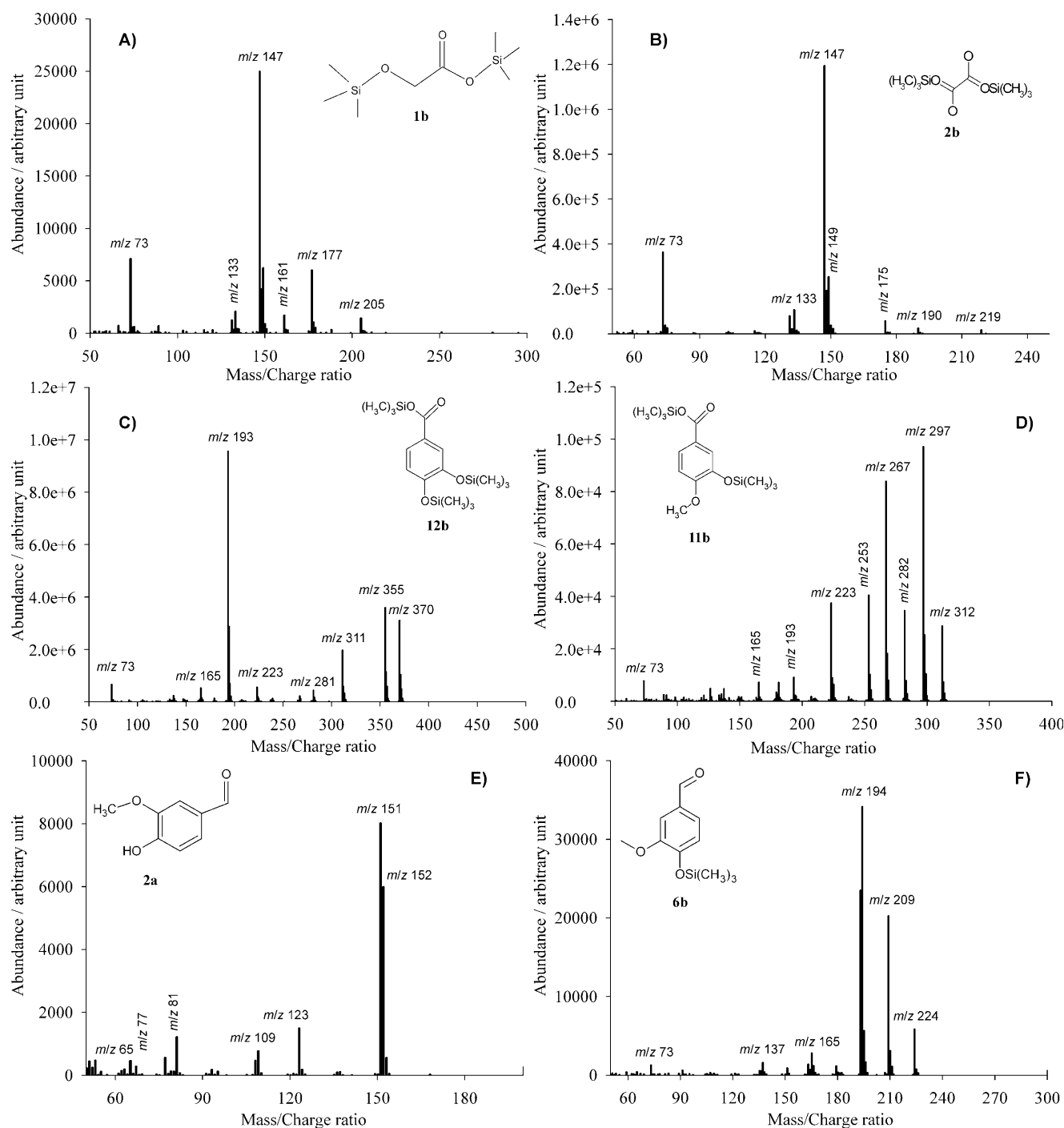


Figure 7. Mass spectra of reaction products confirmed by standard analyses. A) TMS derivative of glycolic acid, B) TMS derivative of oxalic acid, C) TMS derivative of 3,4-dihydroxybenzoic acid, D) TMS derivative of vanillic acid, E) vanillin, F) TMS derivative of vanillin.

gem-diol (hydrate) of the aldehyde function to form a bis(trimethylsiloxy)acetal.^[25,30] Mass spectra of the confirmed products with their structures are illustrated in Figure 7.

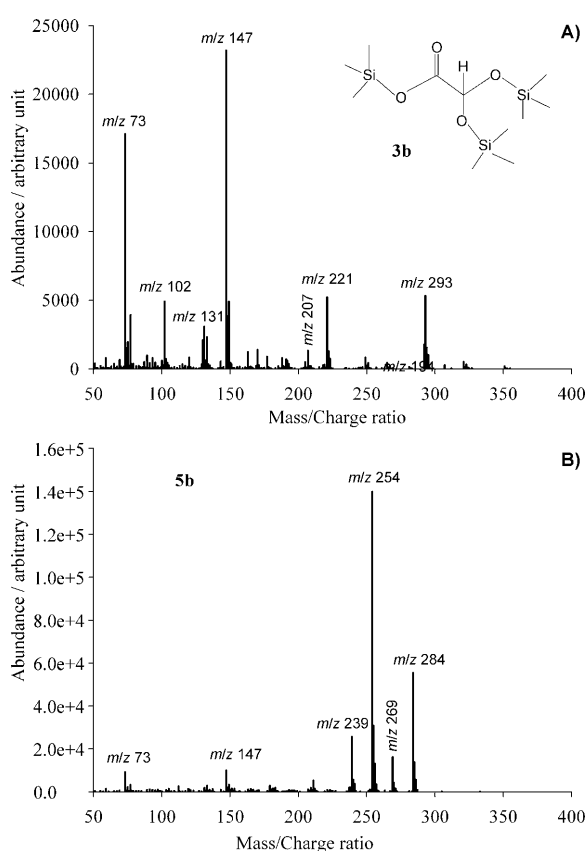
In Table 1 a list of the identified products (numbered from **1b** to **13b** in Figure 6B) with their names, their molecular masses and their retention times is given.

As shown in Table 1, many oxidation products were identified, and most of them were confirmed by their corresponding standards. The reaction product number **3** is suggested as an

acetal artefact of glyoxylic acid which is most probably formed during the reaction of BSTFA with the *gem*-diol of the aldehyde function of glyoxylic acid to form a bis(trimethylsiloxy)acetal.^[30] A mass spectrum of compound **3** in Table 1 is shown in Figure 8A. Unfortunately, some detected oxidation products such as **5** (Figure 8B) could not be identified. Indeed, oxidation product **5** contains two or more OH functions (–OH and/or –COOH) in its structure as these moieties were confirmed by the derivatization of the sample (*m/z* = 147, Figure 8B).

Table 1. Identified products of the reaction of ozone with coniferyl aldehyde. Numbers 1–13 correspond to the numbers in the chromatogram of Figure 6B.

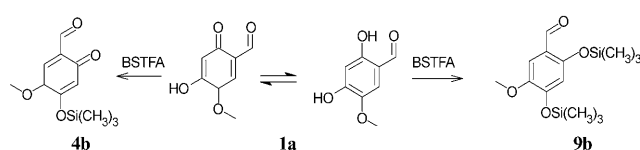
Number	RT [min]	Mw	Mw-TMS	Functions	Identification	Standard confirmed
1b	4.37	76	220	OH + COOH	glycolic acid	yes
2b	4.93	90	234	2COOH	oxalic acid	yes
3b	4.93	90	234	2OH + COOH	glyoxylic acid (its artefact) 4-hydroxy-3-methoxy-6-	no
4b	8.55	96	240	2OH	oxocyclohexa-1,4-diene-1-carbaldehyde	no
5b	8.71	140	284	2OH	unidentified	no
6b	8.88	152	284	OH	vanillin	yes
7b	10.04	152	224	}	vanillin (its artefact)	yes
8b	10.23	152	342			
10b	10.38	152	386			
9b	10.32	168	312	2OH	artefact of (4)	no
11b	10.48	168	312	OH + COOH	vanillic acid	yes
12b	10.77	154	370	2OH + COOH	3,4-dihydroxybenzoic acid	yes
13b	11.21	178	250	OH	coniferyl aldehyde (reagent)	yes

**Figure 8.** Mass spectra of A) artefact of glyoxylic acid and B) unknown compound peak 5.

Following the direct GC-MS analysis one peak emerged at retention time $RT=7.7$ min (peak **1a** in Figure 6A) with $m/z=168$. Its fragment ions $m/z=140$ (M^+-28) in the mass spectrum indicates the probable loss of CO (Figure 9A).

After derivatization of the sample with BSTFA, two peaks with $m/z=240$ (peak **4b**) and $m/z=312$ (peak **9b**) were observed (Figure 6B). These peaks **4b** and **9b** are most probably the corresponding mono- and di-TMS-derivatives of the observed peak **1a** obtained by the direct analysis (Figure 6A). Little reported that ketones with α -hydrogen atoms react to

form artefacts through their enol-form.^[30] The unknown compound with $m/z=168$ which contains CO, CH_3 , OH and $C=O$ can be suggested as 4-hydroxy-3-methoxy-6-oxocyclohexa-1,4-diene-1-carbaldehyde but unfortunately this suggestion cannot be confirmed by a commercial standard. Following the derivatization with BSTFA we suggest the reaction of this unknown product ($m/z=168$) as follows:



2.3. Ozonolysis Mechanism

The reaction mechanism of gas-phase ozone with organic compounds containing $C=C$ bonds is complex, and for many years it has been a focus of interest.^[31–35]

Ozone is known to react with aromatic compounds leading either to a substitution (atom attack) or to a ring opening (bond attack). The location of ozone attack can be correlated with the lowest atom or bond localisation energies of the target compound.^[36] The nature and position of the substituents on the aromatic ring play a key role in the ozonolysis mechanism and strongly influence both the reaction rate and the composition of the oxidation products.^[37] In the last years the gas-phase ozonolysis of alkenes has received renewed attention as it is a source of radicals in the atmosphere. An important number of scavenger^[38–40] and tracer^[40–43] studies indicate that reactions of ozone with alkenes and with the aromatic ring moiety may be a source of hydroxyl radicals. Indeed, these reports have been confirmed by direct OH measurements.^[44–47] Malkin et al. reported that ozonation of isoprene leads to the formation of OH as well as HO_2 .^[48] Moreover, Nunes et al. have shown that the reactions of ozone with aromatic compounds lead to the formation of OH, HO_2 and ring-opened products.^[49] Herein, ring-opened products resulting from the ozone–aromatic compound reaction were not detect-

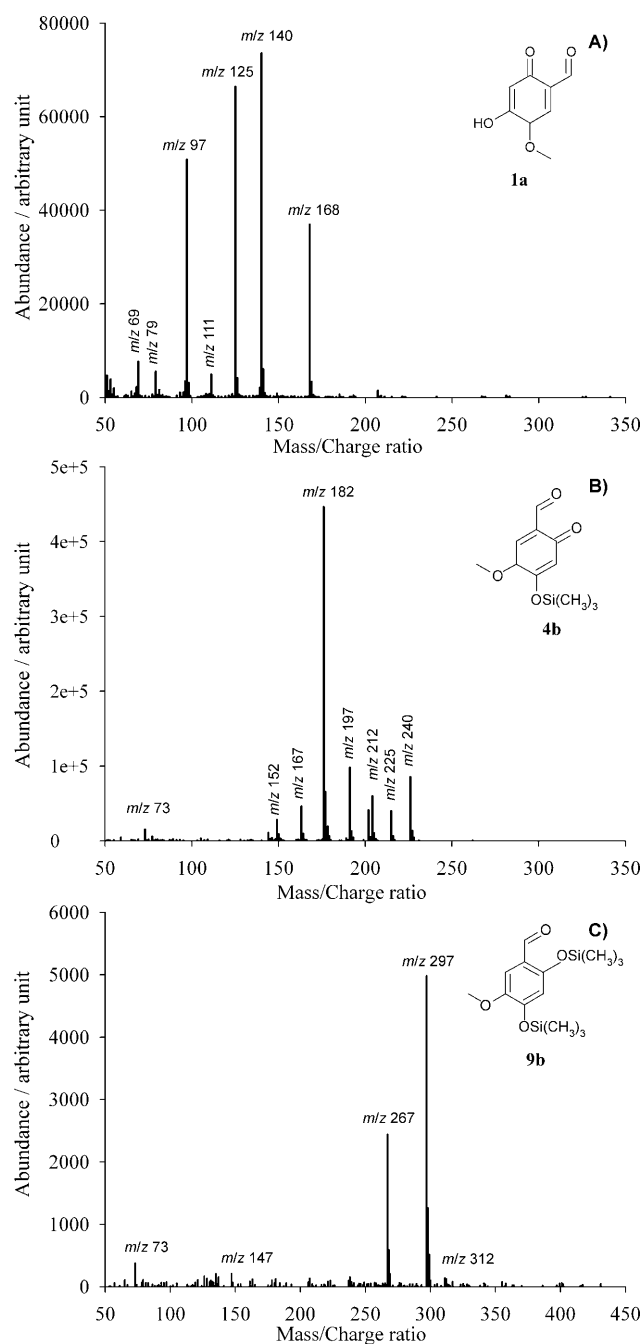


Figure 9. Mass spectra of unidentified oxidation products: A) first peak at $T_R = 7.7$ min in Figure 6A. B) mono-derivative, peak 4 in Figure 6B and C) di-derivative, peak 9 in Figure 6B.

ed. Based on these findings and the reaction products as identified in the present study we can assume that formation of hydroxyl radicals occurs during the ozonolysis of coniferyl aldehyde adsorbed on silica particles.

It was assumed by Martinez and Herron that the formation of OH radicals can result from a 1,4-sigmatropic shift within the Criegee intermediate (CI) followed by bond fission.^[50] This isomerization requires that the alkyl-substituent group is on

the same side of the CI as the terminal O atom (*syn*-conformation).

In this context it should be noted that the ozonolysis of double bonds in alkenes and aromatic rings produce not only radical species but it also leads to oligomerization.^[27] Furthermore, Sadezky et al. have shown that ozonolysis of alkenes may lead to the oligomerization via oligoperoxide formation of small stabilized CI in the gas phase.^[51–52]

Fliszar et al. exhibited that in cases where an organic compound contains both an aromatic ring and a C=C alkene bond the ozone attacks preferentially the C=C bond.^[33] Coniferyl aldehyde contains both an aromatic ring and an unsaturated alkene C=C bond. Therefore, we suggest that the reaction of gas-phase ozone with coniferyl aldehyde proceeds via a concerted cycloaddition process which implies a bridging addition of ozone to the C=C bond as depicted in Scheme 1. The latter process leads to the formation of the intermediate primary ozonide which rapidly decomposes via two pathways to a carbonyl plus a Criegee intermediate. The CI is a carbonyl oxide which can exist in the *syn*- or *anti*-configuration.^[33,53–54] Scheme 1 shows that after rearrangement of the atoms, CI1 yields glycolic acid and glyoxylic acid.

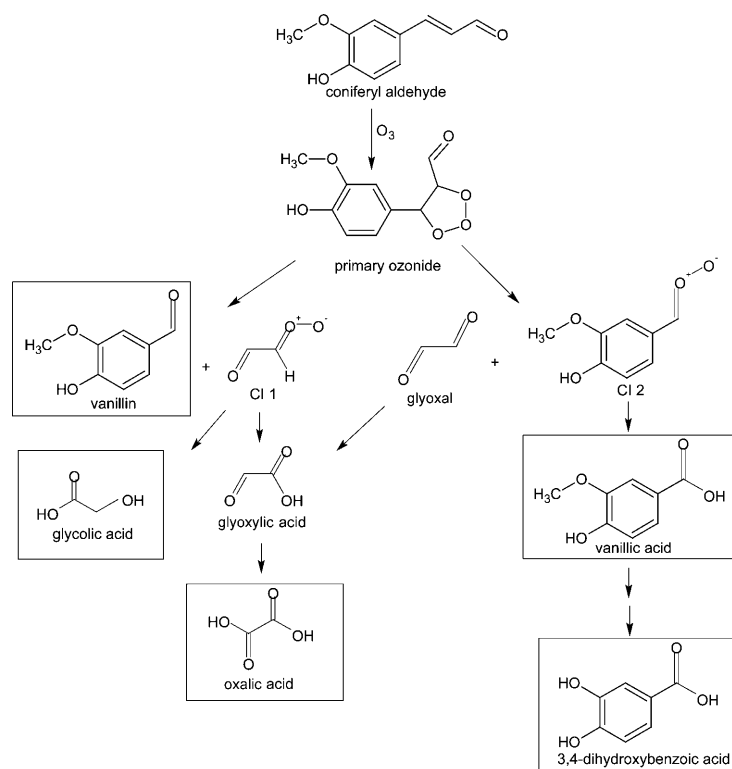
Based on the reaction products identified herein we can assume that formation of hydroxyl radicals occurs during the ozonolysis of coniferyl aldehyde adsorbed on silica particles. The hydroxyl radicals generated during the ozonolysis are involved in the hydroxylation of the produced intermediate products. Hence, the glyoxylic acid is finally converted to oxalic acid by addition of OH to the carbonyl group. Oxalic acid is known as the smallest dicarboxylic acid deposited in atmospheric condensed particles.^[55–57] On the other hand, CI2 leads to vanillic acid which is further oxidized to 3,4-dihydroxybenzoic acid. To the best of our knowledge, there is no previous information available in the literature concerning the mechanism and reaction products of the ozonolysis of coniferyl aldehyde adsorbed on silica particles.

3. Atmospheric Implications and Conclusions

Although there are many studies focused on the heterogeneous reactions of atmospheric relevance, the important light-induced heterogeneous reactions are unknown or incompletely characterized yet, which prevents their inclusion in atmospheric models. Herein, the heterogeneous reaction of gaseous ozone with coniferyl aldehyde adsorbed on silica particle was studied at concentration levels of ozone up to 6 ppm. The reactions were carried out both in total darkness and under simulated sunlight at 297 K. The observed photolytic rate constant implies that the direct photolysis is the predominant reaction of coniferyl aldehyde in atmospheric environment.

The growth of the two main identified products, that is, vanillin and vanillic acid was presented as function of time and ozone concentrations.

Eight reaction products were detected in the reaction with ozone and five of them, that is, glycolic acid, oxalic acid, vanillin, vanillic acid and 3,4-dihydroxybenzoic acid, were identified



Scheme 1.

and confirmed by their corresponding standards. A reaction mechanism has been proposed to explain their formation.

It is noteworthy that the reaction of ozone with coniferyl aldehyde represents a source of OH radicals for the same reasons as the ozonolysis of simpler unsaturated compounds. In addition, these reactions (such as the reaction of ozone with coniferyl aldehyde) can be an important source of secondary organic aerosol (SOA). SOA contains an important quantity of organic acids, such as the ones identified in this study (i.e. glycolic acid, oxalic acid, vanillic acid and 3,4-dihydroxybenzoic acid). It has been demonstrated that these acids serve as nucleation species for aerosol formation and growth.^[58]

Finally, for the conditions of the sunlight spectrum the photolytic lifetime of coniferyl aldehyde in the atmosphere can be estimated to be about four times longer than under laboratory conditions, considering the wavelength range up to 350 nm.

Experimental Section

Chemicals and Reagents: Coniferyl aldehyde (98%), vanillin (99%), vanillic acid ($\geq 97\%$), 3,4-dihydroxybenzoic acid ($\geq 97\%$) and glycolic acid (99%) were supplied by Sigma-Aldrich, 2-methoxyphenol-3,4,5,6- d_4 OD (99.7%) was supplied by CDN Quality Stable Isotopes Chemcats (Canada), and oxalic acid (99.5%, p. a.) was supplied by Merck and used without further purification. Bis(trimethylsilyl)-trifluoroacetamide (BSTFA) was from Sigma-Aldrich and contained 10% trimethylchlorosilane. The SiO_2 powder Aerosil R812 with a purity of $\geq 99.8\%$, average particle size of 7 nm and specific surface of $260\text{ m}^2\text{ g}^{-1}$ was supplied by Evonik (France).

Preparation of the Coating: The coating of the silica particles with coniferyl aldehyde was done by liquid-solid adsorption. The solution of coniferyl aldehyde ($\sim 30\text{ mg}$ in 150 mL of dichloromethane) was mixed with 1.5 g of SiO_2 powder in a pyrex bulb with a volume of 500 cm^3 . This bulb was wrapped with aluminium foil and treated in an ultrasonic bath (Branson 3510, USA) for 30 min to obtain homogeneous particles. Then, the solvent was slowly evaporated at 40°C and $850 \pm 85\text{ mbar}$ within 60 min in the rotary evaporator. The prepared particles were then additionally dried in flowing nitrogen gas for about 15 min before proceeding with the different experimental conditions.

Assuming a uniform surface coverage of the particles, the amount of coniferyl aldehyde adsorbed on the silica particles was below a monolayer: The mass of 1.5 g of silicon dioxide used corresponds to a total surface of 390 m^2 according to the specifications of the supplier. Assuming both a spherical geometry of the molecule and that no volatilization of coniferyl aldehyde occurs during the drying process, 30 mg of coniferyl aldehyde possess a surface of 180 m^2 . This surface was determined as reported in our previous study.^[25] Thus, the percentage of aerosol surface coated with coniferyl aldehyde represents 45% of a monolayer and the average loading of coniferyl aldehyde on the silica particle was $\sim 2\%$ by weight.

Experimental Procedure: About 300 mg of the coated particles ($\sim 6\text{ mg}$ of coniferyl aldehyde) were transferred into another pyrex bulb each for exposure to various ozone mixing ratios ranging from 60 ppb to 6 ppm. The latter was done under dark conditions and in the presence of simulated sunlight. A 300 W xenon lamp (LOT-Oriel) was used to simulate the broadband continuous light emitted from sun. Any output from the xenon lamp with wavelengths shorter than 300 nm was absorbed by a Pyrex filter.

Portions of 300 mg of the dried and coated solid particles were exposed each to simulated sunlight at a distance of 10 cm from the bulb. The rotation of the bulb ensured a homogeneous irradiation of the particles during the whole experiment. Simultaneously, an ozone flux with mixing ratios at 0, 0.06, 0.25, 1, 3 and 6 ppm in air was fed through the bulb. The production of ozone was done with a commercial ozone generator (UVP, LLC Upland, UK). This ozone generator is based on the photolysis of O_2 by the 185 nm radiation of a low-pressure mercury lamp inserted into the radiation housing.

After reaction times of 1, 2, 4, 6 and 8 h at 297 K, the solid particles were solvent-extracted in dichloromethane for 30 min by ultrasonication. Subsequently, the suspended particles were centrifuged (Sorvall Legend Micro 17, Electron Corp., TermoFisher) in order to separate the organic compounds dissolved in dichloromethane from the SiO_2 particles. Then the extracts were filtered with iso-disc filters ($0.45\text{ }\mu\text{m}$, PTFE 25-4, Supelco, USA). Finally, the clear solutions were analyzed by GC-MS for quantification and product identification.

GC-MS Analysis: Spectra of each sample were obtained using gas chromatography combined with mass spectrometry (GC-MS). Analyses were carried out before and after derivatization with BSTFA as reported previously.^[25–27] The extract solutions were analyzed by using electron impact ionization mode (70 eV) according to the following parameters: column THERMO TR-5MS (internal diameter 0.25 mm , length 30 m , film thickness $0.25\text{ }\mu\text{m}$), injection volume

1 μL , inlet temperature 250 °C, interface temperature 330 °C. The following temperature program was used: hold 1 min at 80 °C, increase temperature to 220 °C at a rate of 15 °C min⁻¹, increase temperature to 300 °C at 25 °C min⁻¹, hold 15 min at 300 °C. A Combi PAL autosampler was used to allow automated analyses.

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- [1] R. M. Kamens, G. D. Rives, J. M. Perry, D. A. Bell, R. F., Jr. Paylor, R. G. Goodman, L. D. Claxton, *Environ. Sci. Technol.* **1984**, *18*, 523–530.
- [2] R. Kamens, D. Bell, A. Dietrich, J. Perry, R. Goodman, L. Claxton, S. Tejada, *Environ. Sci. Technol.* **1985**, *19*, 63–69.
- [3] D. A. Bell, R. M. Kamens, *Atmos. Environ.* **1986**, *20*, 318–321.
- [4] T. E. Kleindienst, P. B. Shepson, E. O. Edney, L. D. Claxton, L. T. Cupitt, *Environ. Sci. Technol.* **1986**, *20*, 493–501.
- [5] J. L. Gras, M. D. Keywood, G. P. Ayers, *Atmos. Environ.* **2001**, *35*, 1881–1889.
- [6] G. T. Wolff, R. J. Countess, P. J. Groblicki, M. A. Ferman, S. H. Cadle, J. L. Muhlbaier, *Atmos. Environ.* **1981**, *15*, 2485–2502.
- [7] J. M. Dasch, *Environ. Sci. Technol.* **1982**, *16*, 639–645.
- [8] B. C. Boman, A. B. Forsberg, B. G. Jarvholm, *Scand. J. Work Environ. Health* **2003**, *29*, 251–260.
- [9] P. Forster, P. Ramanswamy, P. Artaxo, *IPCC*, Cambridge University Press Cambridge, United Kingdom/New York, **2007**.
- [10] C. G. Nolte, J. J. Schauer, G. R. Cass, B. R. T. Simoneit, *Environ. Sci. Technol.* **2001**, *35*, 1912–1919.
- [11] J. J. Schauer, M. J. Kleeman, G. R. Cass, B. R. T. Simoneit, *Environ. Sci. Technol.* **2001**, *35*, 1716–1728.
- [12] R. A. Parham, R. L. Gray, in *The Chemistry of solid wood* (Ed.: R. Rowell), Amer. Chem. Soc., Washington DC, **1984**.
- [13] R. C. Pettersen, in *The Chemistry of solid wood* (Ed.: R. Rowell), Amer. Chem. Soc., Washington DC, **1984**.
- [14] W. F. Rogge, L. M. Hildemann, M. A. Mazurek, G. R. Cass, B. R. T. Simoneit, *Environ. Sci. Technol.* **1998**, *32*, 13–22.
- [15] L. D. Savoie, J. M. Prospero, E. S. Saltzman, *J. Geophys. Res.* **1989**, *94*, 5069–5080.
- [16] K. D. Perry, T. A. Cahill, R. A. Eldred, D. D. Dutcher, *J. Geophys. Res.* **1997**, *102*, 11225–11238.
- [17] I. G. McKendry, J. P. Hacker, R. Stull, S. Sakiyama, D. Mignacca, K. Reid, *J. Geophys. Res.* **2001**, *106*, 18361–18370.
- [18] D. M. Tratt, R. J. Frouin, D. L. Westphal, *J. Geophys. Res.* **2001**, *106*, 18371–18379.
- [19] C. C. Lai, S. H. Yang, B. J. Finlayson-Pitts, *Langmuir* **1994**, *10*, 4637–4644.
- [20] T. Moise, Y. Rudich, *J. Geophys. Res.* **2000**, *105*, 14667–14676.
- [21] T. Moise, Y. Rudich, *J. Phys. Chem. A* **2002**, *106*, 6469–6476.
- [22] J. W. Morris, P. Davidovits, J. T. Jayne, J. L. Jimenez, Q. Shi, C. E. Kolb, D. R. Worsnop, W. S. Barney, G. Cass, *Geophys. Res. Lett.* **2002**, *29*, 1357–1360.
- [23] V. Vaida, J. E. Headrick, *J. Phys. Chem. A* **2000**, *104*, 5401–5412.
- [24] T. L. Eliason, S. Aloisio, D. J. Donaldson, D. J. Cziczko, V. Vaida, *Atmos. Environ.* **2003**, *37*, 2207–2219.
- [25] S. Net, S. Gligorovski, S. Pietri, H. Wortham, *Phys. Chem. Chem. Phys.* **2010**, *12*, 7603–7611.
- [26] S. Net, L. Nieto-Gligorovski, S. Gligorovski, H. Wortham, *Atmos. Chem. Phys.* **2010**, *10*, 1545–1554.
- [27] S. Net, L. Nieto-Gligorovski, S. Gligorovski, B. Temime-Roussel, S. Barbati, G. Y. Lazarou, H. Wortham, *Atmos. Environ.* **2009**, *43*, 1683–1692.
- [28] I. M. Skurikhin, *Khim. Pri. Soedin.* **1967**, *3*, 339–344.
- [29] V. M. Burlakov, E. I. Chupka, D. D. Chuvashev, H. V. Ratovskii, L. B. Maksimova, *Chem. Nat. Compd.* **1988**, *24*, 227–235.
- [30] J. L. Little, M. F. Wempe, C. M. Buchanan, *J. Chromatogr. B* **2006**, *833*, 219–230.
- [31] R. Atkinson, J. Arey, *Atmos. Environ.* **2003**, *37*, S197–S219.
- [32] R. Atkinson, J. Arey, *Chem. Rev.* **2003**, *103*, 4605–4638.
- [33] S. Fliszar, Cz. Belzecki, J. B. Chylinska, *Can. J. Chem.* **1967**, *45*, 221–224.
- [34] D. Johnson, G. Marston, *Chem. Soc. Rev.* **2008**, *37*, 699–716.
- [35] P. S. Bailey, *Ozonation in Organic Chemistry*, Vols. I, II, *Organic Chemistry Series Vol. 39*, Academic Press, New York, **1978**.
- [36] E. J. Moriconi, W. F. O'Connor, F. T. Wallenberg, *J. Am. Chem. Soc.* **1959**, *81*, 6466–6472.
- [37] G. A. Galstyan, N. F. Tyupalo, S. D. Razumovskii, in *Ozone and its Reactions with Aromatic Compounds in the Liquid Phase*, Vostochnoukr. National University, Lugansk, **2003**, p. 298.
- [38] R. Atkinson, S. M. Aschmann, J. Arey, B. Shorees, *J. Geophys. Res.* **1992**, *97*, 6065–6073.
- [39] R. Atkinson, S. M. Aschmann, *Environ. Sci. Technol.* **1993**, *27*, 1357–1363.
- [40] G. E. Orzechowska, S. E. Paulson, *Atmos. Environ.* **2002**, *36*, 571–581.
- [41] G. E. Orzechowska, S. E. Paulson, *J. Phys. Chem. A* **2005**, *109*, 5358–5365.
- [42] A. R. Rickard, D. Johnson, C. D. McGill, G. Marston, *J. Phys. Chem. A* **1999**, *103*, 7656–7654.
- [43] J. D. Fenske, K. T. Kuwata, K. N. Houk, S. E. Paulson, *J. Phys. Chem. A* **2000**, *104*, 7246–7254.
- [44] J. H. Kroll, J. S. Clarke, N. M. Donahue, J. G. Anderson, K. L. Demerjian, *J. Phys. Chem. A* **2001**, *105*, 1554–1560.
- [45] J. H. Kroll, S. R. Sahay, J. G. Anderson, K. L. Demerjian, N. M. Donahue, *J. Phys. Chem. A* **2001**, *105*, 4446–4457.
- [46] J. H. Kroll, T. F. Hanisco, N. M. Donahue, K. L. Demerjian, J. G. Anderson, *Geophys. Res. Lett.* **2001**, *28*, 3863–3866.
- [47] M. Siese, K. H. Becker, K. J. Brockmann, H. Geiger, A. Hofzumahaus, F. Holland, D. Mihelcic, K. Wirtz, *Environ. Sci. Technol.* **2001**, *35*, 4660–4667.
- [48] T. L. Malkin, A. Goddard, D. E. Heard, P. W. Seakins, *Atmos. Chem. Phys.* **2010**, *10*, 1441–1459.
- [49] F. M. N. Nunes, M. C. C. Veloso, P. A. de P. Pereira, J. B. de Andrade, *Atmos. Environ.* **2005**, *39*, 7715–7730.
- [50] R. I. Martinez, J. T. Herron, *J. Phys. Chem.* **1988**, *92*, 4644–4648.
- [51] A. Sadezky, P. Chaimbault, A. Mellouki, A. Römpp, R. Winterhalter, G. K. Moortgat, G. Le Bras, *Atmos. Chem. Phys.* **2006**, *6*, 5009–5024.
- [52] A. Sadezky, R. Winterhalter, B. Kanawati, A. Römpp, B. Spengler, A. Mellouki, G. Le Bras, P. Chaimbault, G. K. Moortgat, *Atmos. Chem. Phys.* **2008**, *8*, 2667–2699.
- [53] J. H. Kroll, N. M. Donahue, V. J. C. Kenneth, L. Demerjian, J. G. Anderson, *J. Am. Chem. Soc.* **2002**, *124*, 8518–8519.
- [54] R. Gutbrod, R. N. Schindler, E. Kraka, D. Cremer, *Chem. Phys. Lett.* **1996**, *252*, 221–229.
- [55] A. Chebbi, P. Carlier, *Atmos. Environ.* **1996**, *30*, 4233–4249.
- [56] H. Wang, K. Kawamura, K. Yamazaki, *J. Atmos. Chem.* **2006**, *53*, 43–61.
- [57] I. Grgić, L. I. Nieto-Gligorovski, S. Net, B. Temime-Roussel, S. Gligorovski, H. Wortham, *Phys. Chem. Phys.* **2010**, *12*, 698–707.
- [58] T. S. Christoffersen, J. Hjorth, O. Horie, N. R. Jensen, D. Kotzias, L. L. Molander, P. Neeb, L. Ruppert, R. Winterhalter, A. Virkkula, K. Wirtz, B. R. Larsen, *Atmos. Environ.* **1998**, *32*, 1657–1661.
- [59] SPARC On-Line Calculator: <http://sparc.chem.uga.edu/sparc/>.
- [60] NIST MS search, version 1.7, **1998**.

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