Heterogeneous oxidation of the insecticide cypermethrin as thin film and airborne particles by hydroxyl radicals and ozone

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Evaluation of pesticides’ fate in the atmosphere is important in terms of environmental effects on non-target areas and risk assessments analysis. This evaluation is usually done in the laboratory using analytical grade materials and is then extrapolated to more realistic conditions. To assess the effect of the pesticide purity level (i.e. analytical vs. technical) and state (i.e. sorbed film vs. airborne particles), we have investigated the oxidation rates and products of technical grade cypermethrin as thin film and in its airborne form, and compared it with our former results for analytical grade material. Technical grade thin film kinetics for both ozone and OH radicals revealed reaction rates similar to the analytical material, implying that for these processes, the analytical grade can be used as a good proxy. Oxidation products, however, were slightly different with two additional condensed phase products: formanilide, N-phenyl and 2-biphenyl carboxylic acid, which were seen with the technical grade material only. OH experiments revealed spectral changes that suggest the immediate formation of surface products containing OH functionalities. For the ozonolysis studies of airborne material, a novel set-up was used, which included a long-path FTIR cell in conjugation with a Scanning Mobility Particle Sizer (SMPS) system. This set-up allowed monitoring of real-time reaction kinetics and product formation (gas and condensed phases) together with aerosol size distribution measurements. Similar condensed phase products were observed for airborne and thin film technical grade cypermethrin after ozonolysis. Additionally, CO, CO₂ and possibly acetaldehyde were identified as gaseous oxidation products in the aerosols experiments only. A kinetic model fitted to our experimental system enabled the identification of both primary and secondary products as well as extraction of a formation rate constant. Kinetic calculations (based on gaseous products formation rate) have revealed values similar to that of the thin film experiments. Interestingly, heterogeneous oxidation of cypermethrin was also found to generate ultra fine secondary organic aerosols. Again, no significant difference was observed between analytical and technical grade materials. However, particle size distribution was much broader when films were exposed to OH and ozone than to ozone alone.

Introduction

Pyrethroids are synthetic pyrethrins, which are gaining popularity as replacements for organophosphate insecticides due to their low avian and mammalian toxicity. As such, they are widely used both indoor and outdoor. Having low vapour pressures, these pesticides are likely to reside in the atmosphere in the airborne particulate phase or on stagnant surfaces, such as soil and leaves.¹

While adsorbed on atmospheric interfaces, these compounds interact with solar radiation and atmospheric oxidants, yielding products that may still pose health and environmental concerns (sometimes even more than the parent compound).²,³

In order to model pesticides’ fate in the atmosphere or to conduct risk analysis regarding their influence on non-target communities, there is a need to quantitatively assess their degradation pathways and to acquire knowledge on their degradation products. Our former investigations were focused on the heterogeneous reactions of analytical grade α-cypermethrin, which is a common member of the pyrethroid family. Thin films of the pure material were tested under different ozone concentrations and under UV radiation (254 and 313 nm) at various atmospheric like environments.²,³ However, a question arose whether laboratory analytical grade pesticides can serve as a good proxy for the real materials that are being used in the field (from hereafter referred to as technical grade pesticides). It is long established that pesticides have numerous formulations, which can greatly affect the behaviour of the active material in the field.⁴ Also, as our former investigations were done on thin films, a question remained regarding the difference between the reactivity of thin films and airborne particles (i.e., submicron aerosols).

The main goal of the present study was to gain quantitative insight regarding ozonolysis and OH oxidation of a technical grade cypermethrin, both as a film and in its aerosolized form, and to compare its oxidation rates to that of its analytical grade analogue. In general, quantitative information on heterogeneous ozonolysis of pesticides is limited, and the knowledge...
is even scarcer regarding ozonolysis of airborne pesticides. Such data are clearly needed considering that the previous studies have suggested that deposited and airborne materials may have different reactivities towards gaseous oxidants.\(^5\) Furthermore, most previous investigations regarding oxidation of airborne pesticides conducted off-line analysis of the aerosols after collecting them on filters.\(^6\)–\(^9\) Hence, such investigations did not have real-time capabilities and could not monitor by-products evolution. In the present work we study the heterogeneous oxidation of airborne pesticides using real-time spectroscopic monitoring of both the condensed and gas phases, and compare the behaviour of analytical and technical grade cypermethrin to assess the applicability of laboratory results to the field.

### Experimental

#### Thin films ozonolysis

Detailed description of the experimental procedure regarding cypermethrin thin-film oxidation has been given previously.\(^2\) In brief, deposited cypermethrin thin film was prepared from 100 \(\mu\)l of technical grade cypermethrin (Cymbush, Machteshim Agan Ltd, 1% cypermethrin-C\(_2\)H\(_5\)Cl\(_2\)NO\(_3\)) solution in ethanol (0.1% w/w, similar dilution as in agricultural applications) that was deposited on a ZnSe ATR crystal (HATR, Pike Technologies). The amount of active material (i.e., cypermethrin) applied on the ATR was similar to that in the experiments with analytical grade material.\(^2\) The solvent was let to evaporate, and then the crystal was placed on the FTIR instrument (Bruker, Tensor 27). Reaction monitoring was initiated upon the introduction of ozone flow above the film. Different ozone concentrations (4 \(\times\) 10\(^{13}\)–3 \(\times\) 10\(^{15}\) molecules cm\(^{-3}\)) were generated via \(\mathrm{O}_2\) photolysis (Jelight Inc. model 600) and measured using an ozone monitor (InDevk, 2B Technologies). Absorption spectra of the film were recorded every 2 min, averaging 32 scans at 2 cm\(^{-1}\) resolution and spectral range of 650–4500 cm\(^{-1}\), using a deuterated triglycine sulfate (DTGS) detector.

In a separate set of experiments, aqueous solution of technical grade cypermethrin (0.1% w/w) was sprayed using an atomizer (TSI, Model 3076) on the ATR crystal to allow comparison between different application methods. The material was sprayed for periods of 3–5 min until obtaining absorption signals whose strengths were similar to the aforementioned thin films.

#### Thin films OH oxidation

OH radicals were generated via a dark reaction of 2,3-dimethyl 2-butene (TME, 98%, Aldrich) with ozone.\(^10\),\(^11\) Steady-state OH concentrations were calculated using the Acuchem kinetic program,\(^12\) based on reactants concentration at the entrance of the reaction cell. The OH generation procedure followed the method described by Lambe et al. (2007),\(^13\) and modifications were made according to Pflieger (2009).\(^14\) Initial ozone and TME concentrations were 2–3 \(\times\) 10\(^{14}\) and 8–9 \(\times\) 10\(^{12}\) molecules cm\(^{-3}\), respectively. The TME–\(\mathrm{N}_2\) mixture was introduced to the reaction cell from a Teflon bag (25L) using a peristaltic pump. TME level in the bag was quantified by GC-MS and pre-prepared calibration curve. TME and ozone flows to the reactor were set at 60 cm\(^3\) min\(^{-1}\) each. The resulting OH concentration was calculated to be in the order of 7 \(\times\) 10\(^{7}\) molecules cm\(^{-3}\), and the ozone level remained almost unaffected. Formation of OH radicals was confirmed by oxidation experiments of methyl parathion (neat grade, Supelco) and octadecane (98%, Merck) films, which are not reactive toward ozone.

Due to technical complexity, oxidation by hydroxyl radicals was investigated only with thin films (analytical and technical grade) generated as described above but with only 10 \(\mu\)l of pesticide solution.

### Airborne experiments

#### Experimental set-up

The experimental set-up used for the aerosol kinetic experiments is shown in Fig. 1. Aerosols were generated by atomizing (TSI Model 3076 Atomizer) an aqueous solution of technical grade cypermethrin (0.1% w/w, like in field applications), using dry \(\mathrm{N}_2\) gas flow (2.5–3 \(\times\) 1 \(\times\) 1 \(\times\) 10\(^{-2}\) min\(^{-1}\), and from here after LPM) at a pressure of 20–30 psi (1.5–2 bar). The atomized solution droplets passed through two silica-gel dryers (each 60 cm long) consisting of a fine tubular mesh with an inner diameter (ID) of 1.8 cm, to allow free flow of the aerosol stream within the dryer. To increase water drying efficiency a third dryer made of a Nafion membrane 0.6 m long and 1.8 cm ID (Perma Pure Inc.) enclosed in a 7 cm ID glass jacket was added. A counter-flow of dry \(\mathrm{N}_2\) was passed through the jacket at flow rates between 3 and 3.5 LPM, producing a high relative humidity (RH) gradient that drove the rapid diffusion of gas phase water through the Nafion membrane. After drying (to relative humidity levels of less than 5%), the aerosols were introduced to the Scanning Mobility Particle Sizing (SMPS) system for initial size distribution measurement and then diverted to the long path IR gas cell (model 35V, Infrared analysis Inc., \(V\) = 8.5 l, optical path = 22 m), attached to an FTIR spectrometer (Bruker, Vertex70 with photovoltaic Mercury Cadmium Telluride-MCT detector, with effective range of 850–4500 cm\(^{-1}\)). The SMPS system contains a differential mobility analyzer (DMA, TSI model 3080L) and a condensation particle counter (CPC, TSI 3022A). The generated cypermethrin aerosols showed a log-normal size distribution with geometric standard deviation (\(\sigma_g\)) of 2.2 and count median diameter (CMD) between 0.10–0.13 \(\mu\)m. The total particle counts at the beginning of each reaction were 1.0–2.3 \(\times\) 10\(^5\) particles cm\(^{-3}\).

Aerosol flow of 2–3 LPM was introduced into the long path IR cell through a tube with a wide opening (6 mm) at the cell’s bottom, allowing maximal travel distance to the cell’s exit at its top (see Fig. 1). In addition, a weak \(\mathrm{N}_2\) purge flow (40 cm\(^3\) min\(^{-1}\)) was directed towards the bottom mirror to minimize aerosols deposition on it during the measurements. Relative humidity and temperature were measured inside the FTIR cell using a miniature humidity sensor (AMR, Germany) connected to an Ahlborn Almemo 2390-3 reader. During all experiments the temperature was between 297 and 299 K and the relative humidity was below 6%.

IR absorbance spectra averaged 32 scans per spectrum at 1 cm\(^{-1}\) resolution over the range of 4500–850 cm\(^{-1}\).
Background spectrum was taken under dry nitrogen flow. Following aerosol introduction to the cell, extinction spectra were recorded continuously until the system reached steady state (i.e., until no significant changes in spectral bands were observed). After reaching steady state, the aerosol flow was stopped, and the desired ozone concentration was introduced as detailed in the following section. Additional measurements of the aerosol size distribution were performed just before and after the reaction with ozone using the SMPS system. For these measurements, the drawn volume for the SMPS system was 0.3 LPM and each measurement took 5 min to complete. Before reaction, the introduction of aerosol into the cell was done in a flow through mode, and hence, the large volume drawn from the cell for the size distribution measurement did not have an effect on the aerosols in the cell. After reaction, as the reaction proceeded in a semi-batch mode, aerosols were drawn from the reaction cell with a flow rate of 0.1 LPM, and entered into the SMPS system together with a compensating flow of 0.2 LPM nitrogen to complete the total volume needed for the measurement. The measurement range was 14–800 nm at 64 equidistant logarithmic intervals, in which a number concentration of particles (particle number cm$^{-3}$) was measured.

**Ozonolysis.** For the aerosolized ozonolysis experiments, ozone concentrations ranged between $2 \times 10^{13} - 5 \times 10^{15}$ molecules cm$^{-3}$, prior to its introduction to the IR cell. To achieve the desired ozone concentration in the FTIR cell in a short time and with low dilution of its aerosol-loaded atmosphere, an initial batch injection of 200 ml of concentrated ozone mixture (about two orders of magnitude higher than the needed concentration) was introduced to the FTIR cell prior to the continuous low flow (60 ml min$^{-1}$) of ozone at the required concentration that was used during the whole experiment. Nitrogen purging flow of 40 ml min$^{-1}$ was used to decrease particle deposition on the mirrors as much as possible. Reaction monitoring started immediately after the first ozone injection. Multiple IR scans (specifications detailed above) were taken every minute.

**Off-line chromatographic analysis.** Complementary product analysis using GC-MS was performed on both the film extracts and the aerosol residues collected on glass fibre filter (GF/F 47 mm, Whatman) at the reactor’s outlet. Oxidized film residues were eluted with 3 ml ethanol (BioLab, analytical reagent) and kept refrigerated until analyzed by GC-MS. Blank samples were prepared by eluting unreacted cypermethrin film in the same way.

Cypermethrin aerosols collected during ozone exposure (1–2 h) on the filter at the IR cell outlet were extracted ultrasonically in 5 ml of ethanol for 15 min. Extracts were kept refrigerated until GC-MS analysis. Blank samples were prepared by collecting unreacted cypermethrin particles during the fill-up stage of the IR cell (until reaching steady state, ~1 h). GC-MS analysis was performed on a CP-3800 Varian gas chromatograph with a capillary column (VF5MS, 30 m, 0.25 mm ID, and film thickness of 0.25 μm) attached to a Saturn 2000 mass spectrometer. Oven temperature was varied between 100 and 250 °C, using a ramping rate of 10 °C min$^{-1}$. Injection port temperature was 270 °C run in the splitless mode for the first minute and a split ratio of 1 : 10 afterwards. Helium was used as the carrier gas.

**Secondary organic aerosols (SOA) measurements**

Secondary aerosols formation was examined for both analytical and technical grade cypermethrin films upon exposure to ozone and to hydroxyl radicals, using the ATR-FTIR-SMPS system. Background measurements of airborne particles were
performed by preparing thin films (as detailed previously) and purging the system with pure nitrogen. All background experiments gave very low particle number counts; in the range of 50–100 particles cm\(^{-3}\). SOA formation during ozonolysis was studied under two levels of ozone: 3 \times 10^{12} and 1–2 \times 10^{14} molecules cm\(^{-3}\) (120 ppb and 8 ppm, respectively). The low O\(_3\) concentration was chosen in order to better mimic atmospheric scenarios, whereas the high O\(_3\) experiments were done for comparison with the OH experiments, which involved high O\(_3\) levels, 1–2 \times 10^{14} molecules cm\(^{-3}\), as discussed above. Particle distributions were measured using the SMPS system after mixing the 100 ml min\(^{-1}\) gas flow from the ATR reactor (ozone only or ozone–TME mixture in the case of OH experiments) with 200 ml min\(^{-1}\) of pure nitrogen, in order to achieve the sample flow rate requirements of the SMPS system. Measurements were performed repeatedly for 90–120 min, measuring particulate sizes in the range of 16–350 nm.

**Results and discussion**

**Experimental spectra**

Fig. 2 shows the spectra of cypermethrin analytical and technical grade films (molecular formula is shown in the figure), their difference spectrum, and a spectrum of dry aerosolized technical grade cypermethrin. The main differences between the spectra of the two grades are the broader features of the ether bonds (at 1076 and 1125 cm\(^{-1}\)) of the technical grade material (both in film and airborne spectra), possibly due to the mix of isomers present in the technical grade material (in contrast to the pure \textit{cis} isomer of the analytical grade), and the additional absorption bands at 1512 cm\(^{-1}\) and 1613 cm\(^{-1}\). The latter were attributed to additional materials in the formulation of the technical grade pesticide (\textit{i.e.} the overall composition of the technical grade solution used for this study). In addition, it can be seen that the airborne spectrum is noisier, probably due to residues of water vapour and other solvents inherited from the formulation of the material.

**Impact of purity level (analytical vs. technical grade) on cypermethrin ozonolysis**

Our previous investigation on the ozonolysis kinetic and mechanism of cypermethrin used only analytical grade \(\alpha\)-cypermethrin (a pure mixture of \textit{cis}/\textit{trans} isomers in a ratio of 95 : 5).\(^2\) Here, we present the results for the ozonolysis of a technical grade cypermethrin solution (a mixture of \textit{cis}/\textit{trans} isomers in a ratio of about 65 : 35), with the same formulation (\textit{i.e.}, including other ingredients such as solvents and surfactants) and concentrations as used in agricultural applications. As mentioned above, we have also tested two application methods on the ATR crystal: thin film generated \textit{via} solvent evaporation and \textit{via} aerosol deposition on the surface.

**Thin film kinetics.** Ozonolysis rate constants of thin film cypermethrin were extracted from the fit of the temporal change in absorbance (\textit{i.e.}, peak area) at 920 cm\(^{-1}\).\(^2\) Fig. 3 shows the temporal changes in absorbance of a technical grade cypermethrin film under two different ozone concentrations. Fig. 3a shows degradation of the parent material based on its 920 cm\(^{-1}\) band disappearance, and Fig. 3b and c show product build-up (\(P\) and \(P_{\mathrm{ad}}\) represent product absorbance and product absorbance at the end of reaction, respectively) according to the increasing absorbance at 1740 cm\(^{-1}\) (for both application procedures, with integration done between 1680–1800 cm\(^{-1}\)). As shown, most of the data fit well to an exponential representation, which corresponds to pseudo-first order kinetics, except from a slight deviation in the first 20 minutes (Fig. 3a, open rectangles). This deviation may represent a faster reactivity at the beginning of the reaction, when the film is fresh and contains very little oxidation products that may interfere in further cypermethrin oxidation (\textit{e.g.}, by forming some protection oxidized layer at the film surface). However, one needs to remember that the signal difference at this initial stage of the reaction is relatively small and hence is susceptible to higher experimental error. The observed first-order reaction rate constant \(k_{\text{obs}}\) [s\(^{-1}\)] under various ozone levels are plotted in Fig. 4, and can be fitted with a Langmuir–Hinshelwood (LH) reaction mechanism, as follows:

\[
k_{\text{obs}} = \frac{k_{\text{max}}K_{O_3}[O_3]}{1 + K_{O_3}[O_3]} \tag{1}
\]

where \(k_{\text{max}}\) is the maximal rate at high ozone levels when all surface sites are occupied (\textit{i.e.}, product of the surface second-order reaction rate constant and number of surface adsorption sites), and \(K_{O_3}\) is the Langmuir equilibrium constant of ozone on the surface \((=k_{\text{adsorption}}/k_{\text{desorption}})\). No difference in oxidation rate was observed between thin film generated \textit{via} evaporation and \textit{via} spray deposition. This is not surprising considering the relatively large droplets generated by the sprayer, which created “islands” of material on the surface that act like a
Fig. 3  Kinetics of thin films of technical grade cypermethrin with ozone: (a) degradation rate of the parent material as a dried thin film for the 920 cm\(^{-1}\) band for ozone concentrations of 5.6 \(\times\) 10\(^{14}\) molecules cm\(^{-3}\) (open rectangles), and 2.5 \(\times\) 10\(^{15}\) molecules cm\(^{-3}\) (solid rectangles), (b) product build-up using 1740 cm\(^{-1}\) band for the case of dried thin film under same ozone concentrations as in (a), and (c) product build-up for the 1740 cm\(^{-1}\) band for the case of sprayed cypermethrin aerosols for ozone concentrations of 5.2 \(\times\) 10\(^{14}\) molecules cm\(^{-3}\) (open circles) and 3 \(\times\) 10\(^{15}\) molecules cm\(^{-3}\) (solid circles).

Fig. 4  Observed pseudo first-order rate constants as a function of gas phase ozone for the reaction of technical grade cypermethrin and analytical grade cypermethrin (shown in detail in Segal and Dubowski, 2007).\(^7\) Data were fitted to a Langmuir–Hinshelwood curve, shown in eqn (1). Fit parameters (\(k_{max}\) and \(K_{O3}\)) were (1.0 \(\pm\) 0.4) \(\times\) 10\(^{-3}\) s\(^{-1}\) and (5.1 \(\pm\) 2.0) \(\times\) 10\(^{-16}\) cm\(^3\) molecules\(^{-1}\), respectively, for the technical grade material and (7 \(\pm\) 1) \(\times\) 10\(^{-5}\) s\(^{-1}\) and (4.7 \(\pm\) 1.7) \(\times\) 10\(^{-16}\) cm\(^3\) molecules\(^{-1}\) for the analytical grade material.\(^2\) Error bars represent one standard deviation for repeated sets of experiments (\(n = 3\)).

Fig. 5  (a) Comparison between analytical and technical cypermethrin films before and after a reaction with ozone. Solid lines represent films before reaction. Dotted lines represent films spectra at the end of the reaction after a subtraction of the initial spectra at time zero, and (b) products library spectra (taken from NIST Chemistry WebBook: http://webbook.nist.gov/chemistry/), as detailed in text.

cis-isomer form will tend to react more efficiently than the trans-isomer form.

Thin films products. As seen from Fig. 2, the analytical and technical grade cypermethrin films have some spectral differences, especially pronounced in the additional bands at 1512 cm\(^{-1}\) and 1613 cm\(^{-1}\) in the technical grade film. GC-MS analysis of the original films (i.e., before ozonolysis) indeed revealed the presence of additional compounds within the technical formulations, such as 5-chloro-2-nitrobenzoic acid and bis(2-ethylhexyl)phthalate. The latter can be accounted for by some of the spectral differences between the two films (absorbance at 1613 cm\(^{-1}\)). Fig. 5 shows the spectral region of film. Fitting parameters for the experimental data gave values of (1.0 \(\pm\) 0.4) \(\times\) 10\(^{-3}\) s\(^{-1}\) and (5 \(\pm\) 2) \(\times\) 10\(^{-16}\) cm\(^3\) molecule\(^{-1}\) for \(k_{max}\) and \(K_{O3}\), respectively, where error bars represent one standard deviation values. Although \(k_{max}\) seems a bit faster than the previously obtained values for analytical grade cypermethrin film,\(^2\) \(k_{max}\) of (7 \(\pm\) 1) \(\times\) 10\(^{-4}\) [s\(^{-1}\)] and \(K_{O3}\) of (4.7 \(\pm\) 1.7) \(\times\) 10\(^{-16}\) [cm\(^3\) molecule\(^{-1}\)], as shown in the figure, this difference was not statistically significant. This finding seems to indicate that low volatility ingredients of the technical grade material, while residing on the surface, tend to be unreactive even under high levels of ozone. The fact that the technical grade material contains a mixture of the cypermethrin cis and trans isomers (in contrast to the analytical grade \(\alpha\) cypermethrin) does not seem to affect its reactivity toward O\(_3\). This is not surprising since the primary reaction mechanism of cypermethrin ozonolysis is the cleavage of its terminal double bond,\(^15\) and the surface position of this bond (relative to the gas phase) is likely to be quite similar for both the cis and trans isomers. Nevertheless, the impact may be different in other degradation processes. In cypermethrin photolysis, for example, the cis–trans isomerization is considered as one of the main reaction pathways.\(^3,16\) Following this, cypermethrin in its...
Thin films OH oxidation. OH oxidation experiments were conducted on films only, both for the analytical and technical grades. Due to the high O$_3$ level used in these experiments ([O$_3$] $\sim$ 2 x $10^4$ molecules cm$^{-3}$) and the fact that the heterogeneous reaction of O$_3$ and cypermethrin may also generate OH and other radicals on the surface, it is hard to isolate the contribution of OH radicals to the reaction rate. For both technical and analytical grade materials similar degradation rates of the double bond (i.e., 920 cm$^{-1}$) and slightly faster carbonyl build-up rates under ozone alone were observed (Fig. 6a and b). Nevertheless, clear differences were observed between the OH + O$_3$ and reference O$_3$ experiments in the absorption bands associated with OH functional groups (1640 cm$^{-1}$ and 3200-3600 cm$^{-1}$). The monotonic decrease observed under ozone alone is somewhat inhibited in the presence of OH (Fig. 6c and d). The slight increase observed at the 1640 cm$^{-1}$ region may imply that OH oxidation products may contain diketones or amides connected to a carbonyl moiety.

It is interesting to note that at the immediate start of OH reaction (i.e., when TME was added to the ozone stream) the spectrum of the film showed a large increase in absorbance at the broad region of the OH bands at 3200-3600 cm$^{-1}$ (Fig. 7a). Since the addition of TME to the O$_3$ stream did not cause any change in RH, the observed increase in absorbance at the OH band may imply an initial OH addition to the surface. This initial increase in absorbance was followed by a gradual decrease as reaction progressed. This reduction in
absorbance means that evaporation of some adsorbed water occurred as reference spectra were taken under ambient relative humidity whereas oxidation took place under dry atmosphere. To compare, during ozonolysis experiments the same spectral region has shown only a monotonic decrease in absorbance (Fig. 7b). Fig. 7 shows a gradual decrease with time at the absorbed bulk water region (3400–3600 cm\(^{-1}\)) during both ozone and OH experiments. However, an inhibited decrease is observed around the 3200–3400 cm\(^{-1}\) region only under OH (Fig. 7a), which may represent the formation of phenols or alcohols.

The presence of new OH spectral features (absorbance at 1640 cm\(^{-1}\) and 3200 cm\(^{-1}\)) 25 minutes after the addition of TME to the O\(_3\) flow (i.e., OH formation) may suggest the formation of relatively stable intermediate species upon OH exposure. Nevertheless, this has not been further investigated in the present study.

**Secondary organic aerosol (SOA) formation**

Fig. 8 shows temporal changes in size distributions of aerosol generated during ozonolysis ([O\(_3\)\(_g\)] = 120 ppb) of standard grade (Fig. 8a) and technical grade (Fig. 8b) cypermethrin films. As shown, even under such low ozone concentrations aerosol generation starts almost immediately, within a few minutes, possibly as soon as the first products are starting to emerge. A steady state is reached within 10–20 minutes after initial aerosol formation. In general, SOA formed during ozonolysis of the analytical and technical grade substrates showed similar behaviour, with median distributions ranging between 15–50 nm and maximum particle numbers in the order of 10\(^4\) particles per cm\(^3\). Experiments under very high ozone concentration of 4–8 ppm (which were performed as reference experiments for the SOA generation upon OH oxidation) also showed similar trends with particle numbers as high as 10\(^5\) particles per cm\(^3\) and particle sizes up to 90 nm (data not shown for simplicity reasons only). SOA yield was calculated using the ratio between the amount of aerosol produced (in moles) and the amount of cypermethrin reacted. For this calculation the aerosols were assumed to be composed solely of cypermethrin. Summation of all size distributions over the whole measurement time, multiplying each bin count by its corresponding particle volume, density and molecular mass gave the total aerosol mole production. The total amount of material reacted was calculated based on the reaction rate constants obtained from the ATR-FTIR spectra, and the initial cypermethrin concentration. These calculations gave very similar values for SOA yield under low ozone concentrations for the analytical and technical grade materials, with values of 2.8% and 3.3%, respectively. Under very high ozone concentrations the yields were higher, especially for the technical grade material (18% versus 6.4% for the analytical grade). Results for SOA generation under OH experiments are shown in Fig. 8c and d. Comparing these to the results obtained with ozone only reveals similar particle numbers, but wider particle sizes range (15–170 nm versus 15–90 nm). It is interesting to note that the large burst of SOA generation under the OH experiments started only after a lag time of 25–30 minutes in comparison to a shorter time of 5–10 minutes for the high ozone concentration experiments. This may support our former findings shown in Fig. 6, which showed that during OH experiments some chemical changes occur on the surface after 25 minutes, affecting surface spectrum and SOA formation.

**Ozonolysis of cypermethrin aerosols**

Investigation of airborne particles was conducted only in relation to ozonolysis of technical grade cypermethrin. Fig. 9 shows representative spectra of aerosolized cypermethrin generated by atomizing an aqueous solution of a commercial grade product. The spectra in the figure were obtained after water vapour subtraction from the original spectra. The subtraction procedure was performed using a reference water vapour spectrum generated by atomizing water solution and drying it with the same drying system that was used for the cypermethrin aerosols. Subtraction of water from the 1500–1800 cm\(^{-1}\) region was derived from the relative amount of water vapour calculated based on absorbance in the 3200–3600 cm\(^{-1}\) region by a least square fit of the reference water spectrum to the data. Fig. 9a depicts blank experimental spectra, including the initial airborne cypermethrin spectrum and its spectrum after deposition in the reaction cell (i.e., the LP IR cell) for 2 hours. Fig. 9b shows the spectrum after 1 and 120 minutes of reaction with O\(_3\), and the ozone band at 950–1150 cm\(^{-1}\). All cypermethrin representing bands can be seen clearly in both spectra (i.e. the 1247, 1488, 1587, 1740 cm\(^{-1}\) and the skeleton C–H bands at 2900–3100 cm\(^{-1}\)), as was shown in Fig. 2. The ether bands around 1100 cm\(^{-1}\) (1125 and 1076 cm\(^{-1}\)) can only be seen in Fig. 9a, since in Fig. 9b the ozone band masks this region. The initial spectrum is tilted at the long wavenumber region (> 2500 cm\(^{-1}\)) due to an expected

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**Fig. 7** Temporal absorbance of the CH\(_2\) (marked with a dashed rectangle) and the OH region broad band during the reaction of cypermethrin film with OH radicals (a) and ozone (b). In both cases, the spectrum of unreacted cypermethrin film under ambient atmosphere (RH ≈ 50%) was used as reference spectrum.
Mie scattering effect for particles larger than 0.1 μm.\textsuperscript{18,19} The final spectra (gray curves) in both figures show a decrease in the spectrum tilt, which is attributed to deposition of the large particles on the cell’s walls and to the dilution effect by the small N\textsubscript{2} flow above the mirrors.

Products. Fig. 9b shows typical spectra of airborne cypermethrin upon reaction with ozone. The spectrum at the end of the reaction shows the formation of various carbonyl products around the 1740 cm\textsuperscript{-1} band, together with a clear signal of carbon monoxide (2050–2250 cm\textsuperscript{-1}), carbon dioxide (2250–2450 cm\textsuperscript{-1}), and an additional product with absorbance centred at 2710 cm\textsuperscript{-1} (from here after product A). Product A was observed only in the spectra of oxidized airborne cypermethrin and not in the oxidized thin film spectra, which might suggest that this is a gaseous product attributed to the oxidation of technical grade cypermethrin. Product A absorbance spectrum resembles that of acetaldehyde, an additional gaseous product formed only from the reaction of the technical grade material. In comparison to spectra after deposition only, the scattering effect is even less prominent, probably due to the smaller number of large particles by the end of reaction, and
the generation of very small particles that do not contribute to the scattering effect in the measured spectral region. Visual inspection of the spectra over time (details not shown) has shown that the ozone signal varied slightly during the initial stages of the reaction (i.e. increasing or decreasing with time before reaching a plateau in different experiment repetitions). Hence, a calibration curve for ozone had to be made and the ozone concentration was calculated from the measured spectra throughout each reaction. This allowed an estimation of an average ozone value during each reaction, which was used in the kinetic calculations. It should be noticed, though, that due to the real time monitoring of ozone, its excess amount was validated during all experiments.

GC-MS results of the filters placed at the reactor outlet revealed that 2BCA and FAN were the main identified products, like in the investigation of technical grade film. Fig. 10 shows the carbonyl spectral region during the reaction, where surface products containing various carbonyl functional groups, centred at 1750 cm\(^{-1}\) are shown. It shows three distinct spectral regions, which might represent different products with various carbonyl functionalities. It is to be noted that acetaldehyde has absorbance bands around 1700–1800 cm\(^{-1}\), which might contribute to the absorbance increase in this region. Therefore, this region was divided into three possible product contributors (marked as \(P_1\), \(P_2\), and \(P_3\) in the figure).

**Kinetics.** In the airborne material experiments, the 920 cm\(^{-1}\) band could not be seen clearly due to the interfering ozone band and a relatively large noise in this area. Attempts of using this band as a proxy for airborne cypermethrin decomposition rate, as was done in our former film-investigations\(^2,3\) were not successful. Since no other band of cypermethrin could be used for ozonolysis rate quantification, the formation rates of the products during the reaction were used as proxies instead. This approach was recently used by Nájera et al.\(^20\) in their ozonolysis experiments of maleic and fumaric acids aerosols. However, in contrast to the former,\(^20\) which have used a flow tube and substances with relatively short reaction time (two minutes to completion under their experimental conditions), with our substance at least one hour was needed to form a substantial amount of products. Consequently, the cypermethrin reaction was performed in a semi-batch mode, which resulted in some deposition of the airborne material in the IR cell. Thus, for this semi-batch approach it is obvious that using the straightforward product formation rates to derive ozonolysis decomposition rate of airborne cypermethrin would not give accurate results and will in fact be understimating the reaction rate. Hence, a different analysis approach was developed to relate the observed formation rates of the products to the ozonolysis rate of the parent material. Fig. 11 shows the temporal change in the absorbance areas of the products discussed earlier. As shown in the figure, the increase in products’ absorbance with time follows first order kinetics. In order to extract their formation rates we used a set of differential equations (eqn (2)–(5)), as a model to describe, at least approximately, the processes that take place in the

![Fig. 10](image-url) Expanded view of temporal changes of the carbonyl products spectral region formed during ozonolysis reaction of airborne technical grade cypermethrin with 200 ppm ozone.

![Fig. 11](image-url) Formation rate curves for the condensed and gas-phase products formed during the reaction with airborne technical grade cypermethrin at 200 ppm ozone. Solid lines represent the primary model fitted for each product, and dotted lines represent the secondary model fit, as detailed in text.
reaction cell. Eqn (2) describes the airborne cypermethrin concentration, $[C_{yp}]$, in the reaction cell during the reaction:

$$\frac{d[C_{yp}]}{dr} = -k_{O_3}[C_{yp}] - k_{\text{dil}}[C_{yp}] - k_{\text{dep}}[C_{yp}] - k_{m}[C_{yp}]$$

(2)

where $k_{\text{dil}}$ is the dilution rate constant due to the air exchange rate in the cell (i.e. purging above mirrors and a small constant ozone flow to maintain its concentration), $k_{\text{dep}}$ is the deposition rate constant due to particle deposition in the reaction cell, and $k_{O_3}$ is the pseudo first order ozonolysis rate constant [min$^{-1}$]. Also, despite purging above the cell’s mirrors, we have noticed in our blank experiments that even after a long time (i.e. more than 2 hours, which is the time needed for a full air exchange in the cell) the cypermethrin signal is still observable as 20–30% of the original amount. We concluded that this is, at least in part, a result of deposition on the mirrors, implying that the observed signal is the sum of signals from the suspended and mirror deposited material. The correction term $k_{m}$ was included in eqn (2) to take this effect into account. $k_{\text{dil}}$ and $k_{\text{dep}}$ were summed to yield the parameter $k_{d}$ that is used in the sequel.

In competition with eqn (2), we can describe the cypermethrin signal that is contributed from the deposited material on the mirror, $[C_{yp}]$ as:

$$\frac{d[C_{yp}]}{dr} = k_{m}[C_{yp}] - k_{O_3}[C_{yp}]$$

(3)

The formation rate of any primary product $[\psi^1]$ in our system (from here will be referred as the primary model) can be described by summing the source term of the suspended and mirror deposited cypermethrin, and assuming a first-order degradation process:

$$\frac{d[\psi^1]}{dr} = k_{O_3}[C_{yp}] + k_{O_3}[C_{yp}] - k_{d}[\psi^1]$$

(4)

An additional equation was used to describe the formation rate of a secondary product $[\psi^2]$ in the system (from here after the secondary model), by converting $[\psi^1]$ to $[\psi^2]$ with a reaction rate constant of $k_{O_3}$ to yield the following equation:

$$\frac{d[\psi^2]}{dr} = k_{O_3}[\psi^1] - k_{d}[\psi^2]$$

(5)

Eqn (2)–(5) were solved simultaneously using MATLAB symbolic math toolbox (Matlab R2009b version), which gave the theoretical analytical expression for the primary and secondary products temporal change. When solving for the secondary product model, a decomposition of $[\psi^1]$ by ozone was added to eqn (4) with $k_{O_3}$ as the reaction rate constant for this process. By fitting the reaction parameters (i.e. dilution, deposition and reaction rate constants) using a non-linear optimization procedure, a fit was obtained for each of the products (solid lines in Fig. 11). The cypermethrin band at 3000 cm$^{-1}$, which did not show any reactivity toward ozone (as previously observed),$^2$ was used as a proxy to quantify the $k_{d}$ and $k_{m}$ constants during the ozonolysis reaction. Average values for the above physical parameters were 0.015 $\pm$ 0.004 [min$^{-1}$] and 0.005 $\pm$ 0.002 [min$^{-1}$] for $k_{d}$ and $k_{m}$, respectively. For each experiment (i.e., specific ozone concentration), the parameter set of $k_{d}$ and $k_{m}$ were determined. Then, these values were used as inputs for the second step, which used non-linear optimization to fit the reaction rate parameters for each of the observed products at the corresponding experiment. For the gaseous phase products a slightly different procedure was implemented, using the a priori knowledge of the dilution rate $k_{\text{dil}}$ (0.0085 $\pm$ 0.0005), based on the loss rate of CO$_2$ in reference experiments (i.e. dilution only).

The general procedure of the parameter fitting described above was generated for each of the products and revealed that the primary model fits quite well with all products, where it was best fitted to products P$_1$, P$_3$, CO and CO$_2$, while the secondary product formation model was better fitted to P$_2$ and product A (this fit is shown as dotted lines in Fig. 11). Formation rate constants were calculated using the primary product model approach, as we felt that the secondary model parameter fit had too many degrees of freedom to accurately determine those reaction rates. Formation rates for most products (excluding P$_2$) did not vary dramatically with ozone concentration, as expected under these high ozone levels and the observed Langmuir behavior of this reaction (Fig. 4). Under ozone concentration of $(8.5 \pm 4.5) \times 10^{14}$ molecules cm$^{-3}$ the formation rates of CO, CO$_2$, and product A were $1.6 \times 10^{-4}$, $1 \times 10^{-4}$, and $1 \times 10^{-4}$ [s$^{-1}$], respectively, and $7.5 \times 10^{-6}$, $3.7 \times 10^{-6}$, and $2 \times 10^{-6}$ [s$^{-1}$] for the condensed phase products P$_1$, P$_3$, and P$_b$, respectively. Under all ozone concentrations the formation rates of condensed products were lower than that of the gaseous products. A comparison to the thin film results (Fig. 4) shows that the formation rate of airborne particulate products were smaller by about one order of magnitude. By contrast, the gaseous products (CO, CO$_2$, and product A) have shown formation rates quite similar to those shown in Fig. 4. This can be explained by the fact that the observed rates are calculated based on absorbance of products located only within the path of the IR beam; condensed products generated from wall-deposited material could not be detected, and hence their observed signal led to an underestimation of their formation rates. This was not the case for the gaseous products, since newly formed products were released into the cell’s volume and hence detected. Furthermore, as depicted earlier for technical grade cypermethrin films, formation rates of the carbonyl products may be lower by a factor of two in comparison to the loss rate of the parent material (calculated based on the 920 cm$^{-1}$ band decrease rate). A similar trend is likely to occur for aerosolized material, which will also contribute to the lower rates observed for the formation of aerosolized products.

In summary, based on the formation rates of the gaseous products, it seems that the reactivity of the airborne material is similar to its reactivity on films. However, in the case of the carbonyl products, the observed rate is much lower, which can be attributed to both the slower rate that was observed for the technical grade thin film case, and to the fact that wall-deposited material could not be detected in the present experimental set-up.

Size distributions. Aerosol size distributions were taken before and after the reaction of airborne cypermethrin with ozone. In addition, size distributions were measured on blank
Experiments, where only dilution and deposition effects were involved. Fig. 12 shows a representative series of such measurements; an initial size distribution of cypermethrin aerosol (Fig. 12a), size distribution measured after two hours of dilution and deposition (Fig. 12b), and the distribution measured after two hours of exposure to 90 ppm ozone (Fig. 12c). Fig. 12b shows that during the course of two hours of blank experiment, deposition and dilution led to reduction in total particle amount by two orders of magnitude (from about $1 \times 10^5$ to $1 \times 10^3$ particles cm$^{-3}$). However, as seen from the figure, the general distribution shape remained quite similar, apart from a minor relative increase in the small particles count. This can be explained by the fact that smaller particles have longer deposition time, which could cause this relative increase in number. The more interesting phenomenon could be observed after oxidation, with obvious growth of particles in sizes of 10–50 nm, peaking in the range of 20–30 nm. These results are in agreement with our measurements of SOA formation from ozonolysis of technical grade film (Section 3.4). Furthermore, it can be seen that the total number of particles in the range of 100–300 nm decreased more during exposure to ozone than during the blank experiment, suggesting that the reaction is size selective towards this region. This postulation might need further investigation using the generation of mono-dispersed particles and the separate kinetic investigation for each of the narrow distributions.

Conclusions

This work allowed, for the first time, real time monitoring of the production of condensed and gaseous species during the ozonolysis of an airborne insecticide (i.e. cypermethrin). Through the in situ degradation products monitoring we were able to model and quantify reaction kinetics, in spite of the fact that degradation of parent material was not always detectable under the present experimental set-up. The novel experimental set-up used in this work, utilizing long-path FTIR cell and SMPS system, allowed a broader understanding of the reaction system in terms of atmospheric implications; showing that products partition between gas and condensed phases and that SOA are being generated. The latter is of great concern in terms of health impacts, especially as this pesticide is being used in both indoor and outdoor applications.

Under our experimental conditions, no significant difference was observed between cypermethrin oxidation rates under ozone only in comparison to a combination of ozone and OH radicals. Since both ozone and OH concentrations in the experiments were higher in two orders of magnitude than their ambient concentrations, it might be that the observed behaviour will still be valid outdoors.

Interestingly, no significant difference was observed between ozonolysis rates of cypermethrin film adsorbed on inert surface and of aerosolized material. Oxidation rates were also similar for analytical grade cypermethrin and its technical formulation (as used in the field), but differences were observed between the resulting oxidation products.

Our results suggest that, at least for cypermethrin, laboratory studies conducted with analytical standard films do provide a good approximation for real-life oxidation rates. However, the effect of formulation may be significant on other post-application processes, such as photolysis, and therefore should be further studied. In addition, in order to broaden our understanding in relation to additional outdoor scenarios, more experiments should be performed using various substrates on which the insecticide could be adsorbed.

Summary

In this work we have made a comparison between the oxidation of analytical and technical grade cypermethrin (a widely used pyrethroid insecticide), as well as investigated...
the effect of the insecticide state (film vs. airborne) on its reactivity. This was done in order to better evaluate the use of analytical standards as proxies for real life materials. In general, it was found that ozone oxidation rates do not differ significantly between the analytical and technical grade materials, suggesting that the additives in the technical grade formulation are not reactive towards ozone and that there is no significant difference in the accessibility of the terminal C—C bond to gaseous ozone between the cis and trans isomers of cypermethrin. Nevertheless, steric effects between these isomers may result in different degradation rates in other process, such as photolysis.

The comparison of ozonolysis and OH oxidation did not yield a straightforward quantitative measure in terms of reaction rates, and in fact, under the concentrations used, were in the same order of magnitude. However, differences were observed in reaction products (more phenolic and alcoholic derivatives) and in SOA formation patterns (larger particles with a longer lag time emerge in the presence of OH radicals). Significant SOA generation was observed under all experimental conditions, with a yield of ~3%.

In the comparison between airborne and thin film oxidation kinetics, we have shown through the formation of gaseous products that the reaction rates do not differ significantly between fine aerosols and thin films of cypermethrin. This similarity is likely due to the fact that we have investigated products that the reaction rates do not differ significantly in kinetics, we have shown through the formation of gaseous radicals. Significant SOA generation was observed under all experimental conditions, with a yield of ~3%.

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