Gas phase precursors to anthropogenic secondary organic aerosol: Using the Master Chemical Mechanism to probe detailed observations of 1,3,5-trimethylbenzene photo-oxidation


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Abstract
A detailed gas-phase photochemical chamber box model, incorporating the Master Chemical Mechanism (MCMv3.1) degradation scheme for the model anthropogenic aromatic compound 1,3,5-trimethylbenzene, has been used to simulate data measured during a series of aerosol chamber experiments in order to evaluate the mechanism under a variety of VOC/NOx conditions.

The chamber model was used in the interpretation of comprehensive high (mass and time) resolution measurements of 1,3,5-trimethylbenzene and its photo-oxidation products recorded by a Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer (CIR-TOF-MS). Supporting gas and aerosol measurements have also enabled us to explore the 'missing link' between the gas and aerosol phases.

Model-measurement comparisons have been used to gain insight into the complex array of oxygenated products formed, including the peroxide bicyclic ring opening products (α,β-unsaturated-γ-dicarbonyls and furanones) and the O2-bridged peroxide bicyclic ring-retaining products. To our knowledge this is the first time such high molecular weight species, corresponding to various peroxide bicyclic products represented in the MCMv3.1, have been observed in the gas-phase. The model was also used to give insight into which gas-phase species were participating in SOA formation, with the primary and secondary peroxide products, formed primarily under low NOx conditions, identified as likely candidates.

1. Introduction

Aromatic volatile organic compounds are known to be highly reactive, to have large emission rates and high photochemical ozone creation potentials – substantially contributing to photochemical ozone formation (Derwent et al., 1998). It has been estimated that aromatic compounds, whose major sources are from petrol vehicle exhaust and solvent usage, contribute ca. 10% to global anthropogenic non-methane hydrocarbon emissions (Houweling et al., 1998). In the United Kingdom, models predict that total aromatics contribute ca. 30% to regional ozone production (Derwent et al., 2007). Therefore, it is important to understand the detailed photochemical degradation mechanisms of aromatic compounds, under a variety of atmospheric conditions, for use in air quality models.

Aromatic photo-oxidation mechanisms contain a complex array of reaction pathways leading to a wide range of secondary oxygenated and nitrated volatile, semi-volatile and non-volatile organic products which can partition to the aerosol phase (Calvert et al., 2002). Indeed, photo-oxidation of aromatics has been shown to significantly contribute to anthropogenic secondary organic aerosol (SOA) formation (e.g. Hallquist et al., 2009). However, despite its crucial impacts on air quality, climate and associated consequences for human health (Mauderly and Chow, 2008), SOA physical and chemical properties, composition and formation mechanisms are poorly understood, partly owing to a distinct lack of knowledge with regards to gas-phase precursors (Fuzzi et al., 2006).
In the work presented, a chamber optimised photochemical box model was used to simulate the evolution of 1,3,5-trimethylbenzene (TMB) gas-phase photochemistry during a number of comprehensive simulation chamber experiments in order to evaluate the mechanism used under a variety of VOC/NOx conditions. More specifically, the model was used in the interpretation of data recorded by a Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer (CIR-TOF-MS), a novel instrument used to provide comprehensive, high (mass and time) resolution measurements of the organic gaseous oxidation products formed from the TMB precursor (Wyche et al., 2009). Model-measurement comparisons using such highly detailed simultaneous measurements of the complex array of multi-functional products formed, enables us to pin down the mechanism in detail and can also provide key insight for guiding the directions of future laboratory experiments.

The box model used is based around a detailed TMB degradation mechanism which has been extracted from the Master Chemical Mechanism (MCMv3.1; http://mcm.leeds.ac.uk/MCM). MCMv3.1 is a near-explicit chemical mechanism originally conceived to model ozone formation in Europe but now also employed as a benchmark mechanism in a wide variety of applications where chemical detail is required. The MCM currently describes the detailed gas-phase tropospheric degradation of 135 primary emitted non-methane hydrocarbons (NMHCs) leading to a mechanism containing ca. 5900 species and 13 500 reactions (Jenkin et al., 1997, 2003; Saunders et al., 2003). The update from MCMv3.0 to MCMv3.1 was carried out in order to incorporate recent kinetic and mechanistic improvements in the understanding of aromatic photo-oxidation (Bloss et al., 2005b). MCMv3.1 has previously been evaluated using a high quality, comprehensive chamber dataset designed to focus in on key aspects of the photochemical oxidation of benzene, toluene, p-xylene and TMB (Bloss et al., 2005a). However, although the model/measurement agreement was improved in some areas, significant deficiencies were identified in the mechanisms, in particular concerning the ozone formation potential and oxidative capacity of the aromatic hydrocarbon systems.

The modelling work discussed here both supports and complements the companion paper by Wyche et al. (2009), in which the detailed measurements provided by the CIR-TOF-MS (and other instrumentation) are discussed in greater detail. In combination, the work presented here and in Wyche et al. (2009) provides comprehensive information on the gas-phase photochemical degradation of TMB and the identification of potential gas-phase precursors to SOA formation and growth. More specifically, the model has been used to give insight into which gas-phase species are likely to participate in SOA formation, including the high mass (multi-functional) oxygen-bridged bicyclic ring-retaining and primary ring opening products.

2. Experimental

The experimental section of this work was conducted at the Paul Scherrer Institut (PSI) aerosol chamber facility in Switzerland. This is a temperature controlled indoor chamber comprising a 27 m³ Teflon bag illuminated by four 4 kW xenon arc lamps (Paulsen et al., 2005). The chamber was equipped with a suite of instrumentation, including: standard NOx and O₃ monitors, a Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer (CIR-TOF-MS), using proton transfer reaction (PTR) from the hydronium ion (H₃O⁺) as the ionisation technique, to provide comprehensive gas-phase VOC measurements (Blake et al., 2004, 2009), a Peroxy Radical Chemical Amplifier (PERCA) to provide sum of [HO₂ + RO₂] measurements and two Condensation Particle Counters (CPCs) and a Scanning Mobility Particle Sizer (SMPS) to provide particle number density, size and volume total.

In order to explore the effect of NOx on VOC evolution and SOA formation, a total of seven different experiments were conducted with different initial VOC/NOx ratios. Table 1 gives all the major experimental parameters. During the first part of the study five ‘high (initial) NOx’ experiments were conducted (experiments 1–4 and 6), for which all reagents were injected into the chamber prior to initialisation of the photochemistry. To complement the high NOx experiments, two ‘low NOx’ studies were conducted (experiments 5 and 7), for which only the VOC was injected prior to initialisation of the photochemistry and the NOx was maintained at a low steady state level (6–8 ppbV) throughout the experiment via the continuous injection of HONO. The majority of the work described in this study focuses on experiments 6 and 7 as typical examples of high (initial) and low NOx experiments performed, respectively. For further details regarding the chamber, its supporting instrumentation and the experimental protocol the reader is referred to previous publications (Paulsen et al., 2005; Dommen et al., 2006; Wyche et al., 2009).

3. Model construction

The composition and evolution of the gas phase components of the TMB-SOA chamber system were simulated using a chamber optimised photochemical box model incorporating the comprehensive TMB photo-oxidation scheme extracted from MCMv3.1. The TMB mechanism employed (along with an appropriate inorganic reaction scheme) contains ca. 145 species and 390 reactions.

The box model used in this study also includes a series of ‘chamber specific’ auxiliary reactions adapted from Bloss et al. (2005a) and Zador et al. (2005, 2006) in order to take into account the background reactivity of the chamber. The original auxiliary mechanism of Bloss et al. (2005a) was experimentally optimised for use in MCM model simulations of a series of aromatic photo-oxidation experiments similar to those described here, yet conducted at the European PHOTO-REactor (EUPHORE) in Valencia. The chamber auxiliary mechanism employed contains a number of specific features to account for the effects of the experimental conditions of an atmospheric simulation chamber; specifically the effects of the chamber walls. Primarily, these features consider:

1. The introduction of free radicals from heterogeneous wall reactions
2. (Light dependent) adsorption/desorption of NOx species (including HONO) to/from the chamber walls
3. The off-gassing of various reactive species from the chamber walls, which can contribute significantly to the radical budget of the system and subsequent ozone formation
4. Dilution of chamber trace constituents as bulk gas is added to the matrix in order to compensate for gas removal by instruments
5. Use of xenon arc lamps to simulate the solar spectrum

<table>
<thead>
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<th>Exp. number</th>
<th>Initial [VOC] (ppbV)</th>
<th>Initial [NOx] (ppbV)</th>
<th>VOC/NOx ratio</th>
<th>Relative humidity (%)</th>
<th>Experiment duration (min)</th>
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<tr>
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<td>597</td>
<td>135, 130</td>
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specifically to investigate how these effects vary temporally over a range of conditions, the findings of which are reported in Metzger et al. (2008). From sensitive measurements of HONO in the photo-oxidation of TMB, Metzger et al. (2008) found that the addition of a parameterised (light-induced) heterogeneous NO$_2$ → HONO conversion reaction in the chamber specific auxiliary mechanism significantly improved model performance under a variety of VOC/NO$_x$ conditions. This parameterisation is also included in our MCMv3.1 TMB chamber model and is discussed further in Section 4.1.

The photolysis rate parameterisations used in MCMv3.1 (Saunder et al., 2003) have been adjusted to replicate the photolytic conditions inside the PSI chamber. Measurements of all important photolysis rates have been made in the PSI chamber and the photolysis rate parameterisations have been tuned accordingly (Paulsen et al., 2005; Metzger et al., 2008). In order to take into account inter-experiment variability (e.g. due to degradation and temperature effects on the Xe lamps) monitoring of the photolysis throughout each experiment was carried out through the measurement of $j$(NO$_2$) (Metzger et al., 2008).

Each of the model simulations was initiated with the starting concentrations of each experiment (TMB, NO, NO$_2$, and O$_3$). For the modelling of the low NO$_x$ experiments (experiments 5 and 7) HONO was constrained to 10 ppbV throughout the entire simulation period. All simulations were carried out at a constant temperature of 293 K and 50% relative humidity.

### 4. Results and discussion

#### 4.1. Model-measurement comparison of TMB oxidation and the evolution of the major inorganic species

Fig. 1(a) and 1(b) present the modelled and measured profiles for TMB, NO, NO$_2$ and O$_3$ for experiments 6 and 7, respectively, i.e. typical examples of the ‘high initial’ and ‘low NO’ scenarios described above (see Table 1). From initial inspection of these figures it is clear that the model is able to simulate the oxidation of the precursor TMB with some level of success, with some under prediction in the loss rate, particularly in the latter stages of each experiment, indicating an under prediction in the oxidising capacity of the system.

As exemplified by Fig. 1(a) and (b), the box model was reasonably successful in the simulation of measured NO during both experiments. The modelled and measured NO$_2$ concentration profiles are in good agreement up to the point of peak measured concentration, after which the model overestimates the concentration of NO$_2$ throughout the remainder of each experiment. At most the modelled/measured NO$_2$ ratio was as high as 14 during experiment 6 and ~2.8 during experiment 7. This finding suggests that after the peak in NO$_2$ the model is missing one or more NO$_2$ sinks (even with a heterogeneous conversion reaction for NO$_2$ to HONO included in the model, see later discussion).

During both experiments, although the temporal profiles are reasonable, the modelled O$_3$ was also significantly over predicted. In experiment 6, the simulated ozone profile matched the measurements well up until the peak in measured O$_3$. The model O$_3$ peaked ~50 min later than the measurements with a peak over prediction of ~10%. Under low NO$_x$ conditions in experiment 7, by the end of the experiment, owing to a constant (relatively low concentration) supply of NO$_x$, net O$_3$ production occurred throughout the experiment, therefore no peak was reached. By the end of the experiment the modelled O$_3$ over predicted the measurements by ~60%.

Similar findings regarding the over prediction of simulated NO$_2$ and O$_3$ concentration were reported in the evaluation of this study. For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.
sum of peroxy radicals (i.e. \( \sum (\text{HO}_2 + \text{RO}_2) \)) as measured under low NO_x conditions (see Wyche et al., 2009). However, the model does show a more rapid rise in peroxy radical concentrations than the measurements.

Following similar logic to that of Bloss et al. (2005a) it would seem that in the current study there also exists an under prediction in modelled OH levels towards the latter half of the experiment. A number of possible modifications to the mechanism were postulated and tested by Bloss et al. (2005a) in order to improve the model-measurement intercomparison, such as: (1) inclusion of an OH regeneration channel whereby the yield of OH would be increased without any additional NO to NO_2 conversion; (2) inclusion of a fast reaction between O_3 and an intermediate to produce OH; (3) the addition of a process to convert NO_3 to HO_2 in order to decrease O_3 and (4) inclusion of a heterogeneous process to convert NO_2 to HONO. Inclusion of the latter heterogeneous process improved the model-measurement discrepancies described above by simultaneously increasing radical formation and reducing peak O_3 in the system. However, high HONO concentrations were also predicted which could not be rationalised by the measurements.

In a recent paper the MCMv3.1 TMB mechanism was evaluated using a similar set of chamber experiments to those described here (Metzger et al., 2008). This investigation showed that the MCMv3.1 provides a consistent description of the photo-oxidation of TMB over a range of initial VOC/NO_x conditions, but the same divergences in NO, NO_2 and O_3 as those reported here and by Bloss et al. (2005a) were also noted. Owing to their measurement of significantly higher chamber HONO concentrations (in comparison with the model), the authors postulated that the over prediction of O_3 originates from unknown NO_x chemistry occurring on the chamber walls. Consequently Metzger and co-workers included an additional light-induced, heterogeneous NO_2 (wall/light) \( \rightarrow \) HONO conversion reaction within the chamber specific auxiliary mechanism in order to improve model performance. Such photo-enhanced heterogeneous processes have previously been shown to be important in the laboratory (e.g. Stemmler et al., 2006). Such a strong, light-induced reaction was not included in the simulations of Bloss et al. (2005a,b) but was included in this work (see Section 3).

As discussed above, strong evidence exists for the occurrence of a photo-sensitised heterogeneous conversion of NO_3 to HONO in chamber studies on the photo-oxidation of TMB. However, it is unclear how much of this process takes place on the chamber walls and how much occurs in-situ on the photochemically produced SOA surface. Even with the 'PSI parameterised' version of this reaction included in the current model, OH levels (inferred from the divergence in the decays of the measured and modelled TMB profiles) are still underestimated towards the latter half of the experiments. The majority of the discrepancies observed between modelled and measured data occur after the nucleation event has taken place; indeed the magnitudes of all discrepancies noted appear to increase with total aerosol volume. This finding seems to imply, therefore, that SOA may constitute an additional heterogeneous OH radical source.

4.2. Model-measurement comparison of the formation of gas phase organic oxidation products

Figs. 3 and 5–11 give the modelled and CIR-TOF-MS measured profiles of several major TMB photo-oxidation products including 3,5-dimethylbenzaldehyde, 2,4,6-trimethylphenol, a ring-retaining O_2-bridged ketone, a ring-retaining O_2-bridged nitrate, a series of major (isobaric) ring opening compounds, methyl glyoxal, PAN and HCHO. The error limits shown on the data points in each figure give the sum of all quantifiable uncertainties associated with each measurement (generally \( \leq 30\% \)). It should be noted that for certain oxidation products no calibration material was available, hence, a structurally similar surrogate was employed instead (Wyche et al., 2009). In these instances the error margins presented constitute a lower limit. In the majority of cases the modelled and measured profiles for the major organic photo-oxidation products are in good agreement in terms of temporal behaviour and/or concentration magnitude, under both high and low NO_x conditions, giving us confidence in the MCMv3.1 TMB photo-oxidation scheme. However, some discrepancies do exist, as discussed in more detail below.

4.2.1. Aromatic ring-retaining products

Two of the first oxidation products to appear in the TMB mechanism are 3,5-dimethylbenzaldehyde and 2,4,6-trimethylphenol (see Fig. 6 in Wyche et al., 2009). As can be seen in Fig. 3(a) and (b) the evolution and magnitude of both ring-retaining products are simulated reasonably well using the box model. However, at the start of both experiments 6 and 7 there exists a generally more rapid rise in the measured concentrations of both compounds when compared to simulated values. This result possibly implies a slight over prediction in the loss rate of both of these primary products within the model during the initial stages of the experiment or their yields are under predicted in MCMv3.1. Furthermore, there also exists a discrepancy between modelled and measured data during the concentration plateau for 2,4,6-trimethylphenol in the latter half of the experiment under high NO_x conditions. This discrepancy may result from incorrect simulation of production vs. loss of 2,4,6-trimethylphenol in MCMv3.1, however, it may also be a consequence of the formation of an unidentified oxidation product of identical molecular mass during the latter half of the experiment.

Fig. 3. Model-measurement comparison of the temporal evolution of 3,5-dimethylbenzaldehyde (circles) and 2,4,6-trimethylphenol (triangles) during (a) high NO_x experiment 6 and (b) low NO_x experiment 7. Line and coloured markers – model data, open markers with error bars – CIR-TOF-MS measured data. Error limits give the sum of all quantifiable uncertainties associated with each measurement.
gas-phase photo-oxidation of aromatics. The fact that these masses correspond to stable multi-functional oxygen-bridged species in the MCMv3.1 provides compelling evidence for their existence. Owing to the fact that these O_2-bridged type compounds have not been previously detected within the gas-phase and that no reliable calibration factor or kinetic data have yet been derived for such species, a structurally similar proxy calibrant (m-tolualdehyde) was employed in an attempt to put their concentration profiles onto a more quantitative basis. Although the surrogate calibration factor for the O_2-bridged compounds is not expected to give a truly accurate measured concentration, it provides a rough guide. Consequently, it is not possible to make a direct comparison between the magnitude of the measured and modelled concentrations of the O_2-bridged nitrate and ketone. However, as can be seen in Figs. 5 and 6 for experiment 6 and 7, respectively, despite not being on the same quantitative base, the MCMv3.1 chamber model simulated profiles for both TM135BPNO3 and TM135OBPOH agree remarkably well with their experimentally determined equivalents.

In general, owing to the specific levels of NO, HO_2 and RO_2 early in each experiment, the O_2-bridged nitrate was amongst the first of the photo-oxidation products of TMB to appear in the chamber matrix in both the measured and modelled data, under both high and low NO_x conditions (see Fig. 5). Furthermore, TM135BPNO3 also appeared prior to nucleation in both experiments (see Wyche et al., 2009). During the high NO_x experiments TM135BPNO3 remained in a state of production while NO was present within the chamber before its profile was observed to decay as its rate of loss via oxidation (and/or loss to the aerosol) overtook its rate of production, as the precursor TMB was consumed and as [NO_3] fell towards zero. During experiment 6 both the modelled and measured profiles for TM135BPNO3 rose steadily after the lights were switched on to reach a (simulated) peak of ~15.5 ppbV after ~260 min. As the chamber contents evolved and as levels of HO_2 and RO_2 began to increase, other reaction channels became competitive and the O_2-bridged ketone (TM135OBPOH) and peroxide (TM135BPOOH: see below and Section 4.3) were produced. TM135OBPOH and TM135BPOOH appeared at ~65 (Fig. 6(a)) and ~130 (Fig. 12(a)) min, respectively, before continuing on a steady rise throughout both experiments as HO_2 and RO_2 became more prevalent within the chamber. The modelled and measured profiles for TM135OBPOH rose more gradually than TM135BPNO3, up to a modelled value of ~9.7 ppbV after 450 min. The modelled profile for TM135OBPOH does not reach a peak during the timeframe of the simulation (even after 10 h).

Under low NO_x conditions TM135BPNO3 and TM135OBPOH were observed to form more rapidly relative to the high NO_x
scenarios (and achieved peak values earlier) in both the model and experiment (see Fig. 5(b) and Fig. 6(b), respectively). TM135BPN03 was measured to reach its concentration peak more rapidly than was observed in the model, at ~175 rather than ~275 min. From the model simulation, the O_2-bridged nitrate achieved a maximum concentration of 3.7 ppbV during experiment 7. The measured and modelled profiles for TM135BPOOH exhibited very similar behaviour to one another, i.e. a gradual rise in concentration with time, suggesting a state of net production throughout the majority of the experiment. Both modelled and measured profiles for TM135BPOOH peaked after ~485 min under low NOx conditions, with a simulated maximum concentration of 8.3 ppbV.

Negligible amounts of the O_2-bridged diol, TM135BP2OH (structure (D) in Fig. 4), were formed in the MCMv3.1 simulations (<0.3 ppbV under high and low NOx conditions) and its corresponding molecular ion (i.e. MH^+) was not observed in the CIR-TOF-MS data. An appreciable ion signal, corresponding to its dehydrated form was however measured during most experiments, yet potential interference from other species of this molecular weight may exist in this particular channel. The hydroxy peroxide bicyclic peroxide, TM135BPOOH (structure (E) in Fig. 4), is predicted to form in appreciable amounts under both high and low NOx conditions. However, such peroxides are not easily measured using the PTR ionisation technique, primarily owing to substantial post ionisation fragmentation. As a result, no ion corresponding to the protonated O_2-bridged peroxide was measured (Wyche et al., 2009).

4.2.3. Peroxide bicyclic ring opening products

Under atmospheric conditions TMB degrades mainly through the peroxide bicyclic ring opening route (pathway leading to the alkoxy radical (F) in Fig. 4, see also Fig. 6 in Wyche et al., 2009; Calvert et al., 2002). The ring opening chemistry for TMB in the MCMv3.1 is based on only a limited number of experimental studies and by analogy to similar chemistry occurring in other (more studied) alkyl substituted benzene systems. In general, aromatic ring opening chemistry leads to the production of a complex array of oxygenates of varying reactivity and stability, which provide an important source of new radicals during the course of each experiment. TMB can decay (in the presence of O_2) via various peroxide bicyclic intermediates to yield methyl glyoxal as a primary ring opening product along with a furanone and the \( \alpha,\beta \)-unsaturated-\( \gamma \)-dicarboxyl 2-methyl-4-oxo-2-pentenal (and HO_2) as co-products. A variety of possible furanones can be formed in the decomposition process including 3,5-dimethyl-5(2H)-2-furanone, 3,5-dimethyl-3(2H)-2-furanone and 3-methyl-5-methylene-5(2H)-2-furanone (Smith et al., 1999). In the MCMv3.1 only 3,5-dimethyl-5(2H)-2-furanone is produced. Secondary products including citraconic anhydride (3-methyl maleic anhydride), methyl glyoxal and 3,5-dimethyl-5(2H)-2-furanone (from photolysis) are produced from the photo-oxidation of the 2-methyl-4-oxo-2-pentenal in the MCMv3.1. Hamilton et al. (2003) used comprehensive two-dimensional gas chromatography in order to identify the oxygenated photo-oxidation products from the reaction of a series of alkylbenzenes. For TMB, Hamilton et al. only identified three products, 3,5-dimethylbenzaldehyde, 3,5-dimethyl-5(2H)-2-furanone and 3-methyl-5-methylene-5(2H)-2-furanone, with technical difficulties preventing the identification and quantification of various other key oxygenated products (e.g. 3,5-dimethyl-3(2H)-2-furanone is potentially seen but it co-elutes with TMB).

Fig. 7 gives the model-measurement comparison of the temporal evolution of methyl glyoxal during experiments 6 and 7 (i.e. high and low NOx, respectively). In both experiments, the CIR-TOF-MS signal attributed to methyl glyoxal (m/z = 73) was
calibrated using the sensitivity for a structurally similar surrogate (methacrolein). During both experiments the modelled methyl glyoxal concentration/time profiles agree very well with their measured counterparts giving us a degree of confidence in our current understanding of the primary ring opening chemistry forming methyl glyoxal in the MCMv3.1 TMB oxidation scheme.

Fig. 8 shows the concomitant model-measurement comparison of the temporal evolution of various other major ring opening products formed in experiment 6 and experiment 7. As described above the ring opening products 3,5-methyl-5(2H)-2-furanone, 2-methyl-4-oxo-2-pentenal and 3-methyl maleic anhydride are all formed in the MCMv3.1. These compounds are nominally isobaric with a molecular weight of 112; consequently, using the CIR-TOF-MS technique, they may only be measured together in the form of a combined signal of their respective (protonated) parent ions at \( m/z = 113 \) (i.e. \( MH^+ = 112 + 1 \)). For experiment 6 (Fig. 8(a)) the calibrated \( m/z \) 113 temporal profile agrees well with that of the sum of MCMv3.1 ring opening products simulated within the box model; the compounds forming rapidly and peaking after \( \sim 175 \) min at a concentration of \( \sim 64 \) ppbv. After reaching its concentration peak, the measured \( m/z \) 113 profile decayed more slowly than the concomitant modelled profile, with both traces reaching approximate steady state concentrations after \( \sim 400 \) min. The measured \( m/z \) 113 compounds were observed to decay to a plateau at a slower rate than was predicted by the model; moreover, the measured concentration plateau was almost two fold greater than that of the simulation. A potential reason for this discrepancy in the plateau concentration may be that the MCMv3.1 includes only three of the four compounds believed to occupy the \( m/z \) 113 channel; the formation of 3,5-dimethyl-3(2H)-2-furanone is not considered (Smith et al., 1999; Hamilton et al., 2003). In order to ascertain the contribution of 3,5-dimethyl-3(2H)-2-furanone and 2-methyl-4-oxo-2-pentenal to the \( m/z \) 113 channel in this regard, further, speciated measurements are required. The slower decay observed in the measured \( m/z \) 113 signal could also result from the fact that the photochemistry of 3,5-methyl-5(2H)-2-furanone and 2-methyl-4-oxo-2-pentenal within the model is too fast (or their relative contributions are different).

Similar results are shown in Fig. 8(b) for low NOx experiment 7. Both the modelled and measured profiles for the total \( m/z \) 113 ring opening products evolved more rapidly in experiment 7 than in experiment 6, yet reached their respective concentration peaks later. Interestingly, converse to the high NOx scenario, the model overestimates the magnitude of the measured \( m/z \) 113 compounds in the latter half of experiment 7, suggesting that under low NOx conditions there may be potential under prediction in the simulated loss of either 3-methyl maleic anhydride, 2-methyl-4-oxo-2-pentenal or 3,5-dimethyl-5(2H)-2-furanone (possibly to aerosol). Looking at Fig. 8(b) in more detail, it is possible to see that the measured \( m/z = 113 \) signal profile reached a concentration peak of \( \sim 22 \) ppbv after \( \sim 145 \) min, whereas the simulated profile reached a peak concentration of \( \sim 24 \) ppbv, yet much later at between 375 and 415 min. Despite this discrepancy, there exists a high level of agreement between the modelled and measured data in this case (within measurement error). The simulated early and rapid rise in ring opening products for experiment 7 is primarily driven by the formation of 3,5-methyl-5(2H)-2-furanone. Although the branching ratios for the formation of 3,5-methyl-5(2H)-2-furanone and 2-methyl-4-oxo-2-pentenal are the same in MCMv3.1, 2-methyl-4-oxo-2-pentenal reacts more quickly with OH and is also photolysed to form 3,5-methyl-5(2H)-2-furanone as a photoproduct. As discussed in Section 4.3 and in detail in Wyche et al., 2009, ring opening compounds such as the \( m/z \) 113 species and methyl glyoxal may play an important role in the formation and/or growth of SOA.

It is interesting to note that under both high and low NOx conditions, the secondary ring opening product 3-methyl maleic anhydride is only formed in any appreciable amounts in the simulation during the later stages of the experiment. Therefore secondary methyl glyoxal formed as a co-product will also be low and hence the majority of the modelled methyl glyoxal in Fig. 7 originates from the primary ring opening step. This observation was made by Volkamer et al. (2001) in a study of the formation of secondary glyoxal in the toluene system and their findings were used to update secondary aromatic chemistry in MCMv3.1.

4.2.4. Other oxidation products

As can be seen from Figs. 9–11 good agreement was obtained between the simulated and measured profiles for various other significant oxidation products of TMB. Indeed, Figs. 9 and 10 demonstrate that MCMv3.1 is not only simulating primary and secondary products with some degree of success, but it is also able to successfully simulate end stage products such as formaldehyde and peroxyacetyl nitrate (PAN). As PAN \( (m/z \) 46) was observed as the NO\(_2\) fragment ion (Hansel and Wisthaler, 2000), its measured concentrations are reported in terms of signal (normalised counts per second, ncp) rather than mixing ratio units. It should be noted that certain other organic nitrates may also yield the NO\(_2\) ion under protonation in the CIR-TOF-MS and thus contribute to the signal attributed to PAN, however the gas phase concentrations of these other compounds are expected to be somewhat lower than PAN in the current experiments.

Fig. 11 displays the model-measurement profiles for the sum of the secondary products 2-methyl-4-oxo-pent-2-enolic acid
(MCM designation: C5CODBCO2H) and 3-acetyl-2-methyl-oxirane-2-carbaldehyde (MCM designation: EPXMALKT), formed from the ring opening (via 2-methyl-4-oxo-2-pentenal) and epoxide routes, respectively (Calvert et al., 2002). C5CODBCO2H and EPXMALKT are isobaric, hence their respective protonated parent ions are measured together at m/z 129 using the CIR-TOF-MS technique. The measured temporal profiles of the m/z 129 signal agree well with the modelled profiles of C5CODBCO2H + EPXMALKT for both experiments. As the fragmentation behaviour of C5CODBCO2H and EPXMALKT in the CIR-TOF-MS is not well characterised, the measured signals have been presented in units of ncps.

A number of other simple organic acids were also measured within the gas phase, including hydroxy acetic acid (m/z 77), acetic acid (m/z 61) and formic acid (m/z 47) appearing in the chamber ~20–200 min after lights on (see Wyche et al., 2009). Also, enhanced yields of these small organic acids were observed under low NOx conditions. Evidence exists that suggests organic acids play a role in aromatic SOA formation. Fisseha et al. (2004) observed significant quantities of gas and aerosol phase organic acids from the oxidation of TMB in the presence of NOx, more specifically they attributed 20–45% of the total aerosol mass to organic acids. However, such small organic acid products are not formed in any appreciable amounts in the MCMv3.1 simulations, with acetic acid only formed in the latter stages (~4.3 ppbV after 600 min in experiment 6, coming predominantly from the photolysis of methyl glyoxal). It should also be noted that small quantities of formic and acetic acid have also been observed to form or desorb from the chamber walls during chamber ‘blank’ experiments (Metzger et al., 2008).

4.3. Linking the temporal evolution of TMB photo-oxidation products to SOA formation

From the evidence presented here and in the companion paper by Wyche et al. (2009), namely the different temporal behaviour of the TMB photo-oxidation products under different VOC/NOx scenarios (coinciding with a shift in nucleation time) and enhanced product yields under low NOx conditions (coinciding with an enhanced SOA yield), it appears that there exists a role for both the O2-bridged species and primary ring opening compounds (m/z 113) in the growth of TMB-SOA. Certainly the O2-bridged nitrate (TM135BPNO3) and ketone (TM135BPOH), as well as the m/z 113 ring opening products (and the co-product methyl glyoxal) were present within the chamber prior to nucleation (forming more rapidly in the low NOx case) and hence were available to contribute to aerosol mass, either by direct partitioning or via the formation of more condensable species following further oxidative processing. Indeed, correlation plots shown in Wyche et al. (2009) of gas phase mass ‘lost’ and SOA mass produced indicate that the O2-bridged nitrate and the m/z 113 ring opening products contribute to SOA growth (Ng et al., 2007). However, from the data obtained, it appears that the presence of certain other low volatility organic species may be required to initiate the homogeneous nucleation process.

As was discussed in Wyche et al. (2009), there exists evidence to show that organic hydroperoxides may play a significant role in SOA formation and subsequent growth (e.g. Johnson et al., 2005; Hallquist et al., 2009). The most dominant organic hydroperoxide available early on in the chamber matrix is the O2-bridged peroxo radical (TM135BPPOH, compound (E) in Figs. 4 and 13), formed from reaction of the parent O2-bridged peroxy radical (TM135BPPOOH, compound (A) in Fig. 4) with HO2. No direct measurements of the peroxy bicyclic peroxide were made within this study owing to poor ionisation of such species using the proton transfer technique. However, its temporal profile as simulated by the chamber box model is shown in Fig. 12(a) and (b), for both high (initial) and low NOx conditions (experiments 6 and 7, respectively). Also given in Fig. 12 are the SOA number density data (as recorded by the CPC) and the modelled profiles for two further significant organic peroxides observed to form within the chamber simulations;
3-hydroperoxy-4-hydroxy-3,5-dimethyldihydrofuran-2(3H)-one (MCM designation: MXYFUOOH) and 4-hydroperoxy-2,4,5-trimethyl-5-oxotetrahydrofuran-3-yl-nitrate (MCM designation: NMXYFUOOH). Both MXYFUOOH and NMXYFUOOH (structures (F) and (G) in Fig. 13) are produced during the oxidation of TMB from the primary ring opening product 3,5-dimethyl-5(2H)-2-furanone.

The data presented in Fig. 12(a) and (b) provide crucial information for the identification of potential nucleating species in the TMB system. From the combined modelled and measured data, it is possible to see that in both experiments 6 and 7 the onset of nucleation coincides with the simulated appearance of the low volatility O₂-bridged primary peroxide (TM135BPOOH) as the system enters a low NOx state. The modelled profiles of the O₂-bridged peroxide suggest that it would have been formed in significant concentrations within the gas phase, with maximum (simulated) values of ~15 and 6 ppbV for experiments 6 and 7, respectively (i.e. YVOC ~6.9% for experiment 6 and 12.1% for experiment 7). Also, from Fig. 12(a) it appears that in experiment 6 both MXYFUOOH (YVOC ~0.2%) and NMXYFUOOH (YVOC ~3.1%) also appear just prior to nucleation. These findings, combined with peroxy radical measurements and results obtained from partitioning theory described in Wyche et al. (2009), provide compelling evidence that primary and secondary peroxides play an important role in SOA formation during the oxidation of TMB, and potentially during the oxidation of various other aromatic compounds. As nucleation occurred, under both high and low NOx conditions, only once the O₂-bridged primary peroxide had appeared in the chamber model (as [NO] tended to zero), it seems that these compounds may be particularly important in initiating nucleation. Furthermore, the three organic peroxides TM135BPOOH, MXYFUOOH and NMXYFUOOH were also determined to constitute significant contributors to the simulated aerosol mass in the study of Johnson et al. (2005), who employed a gas-phase oxidation model incorporating the MCMv3.1 TMB mechanism coupled to an
absorptive aerosol transfer scheme in order to estimate which semi-volatile products were able to partition to the aerosol phase and hence were available to contribute to aerosol formation/composition. Hydroperoxides can react with species containing an aldehydic functionality to form stable peroxy hemiacetal species (ROOH + HC(=O)R → ROOC(OH)R/ROH). Johnson et al. (2005) included a simple representation of peroxy hemiacetal formation in chamber simulations of the toluene photo-oxidation system and found that the magnitude of the scaling factor required to match simulated aerosol mass concentrations to that observed experimentally was significantly reduced.

From close inspection of results obtained from the box model presented in Fig. 5(a) and (b), it can be seen that the simulated and measured profiles of the O2-bridged nitrate only diverge after nuclelation has occurred (at 184 and 22 min for experiments 6 and 7, respectively). It is possible that the ‘missing mass’ from the simulation may result from partitioning of the O2-bridged nitrate to the aerosol phase, which is not considered within the model. Although this observation may in part be due to aerosol formation, inaccuracies in the TM135BNO3 + OH rate constant and/or the under prediction in modelled [OH] are most likely the dominating factors here. However, Stroud et al. (2004), using the MCMv3.0 toluene gas phase mechanism coupled to an aerosol transfer scheme, found that multi-functional organic nitrates, including the O2-bridged equivalent of TM135BNO3, comprised a significant fraction of their simulated aerosol mass.

One further compound which may contribute to new particle formation/growth in this instance is the O2-bridged ketone (TM135OBPOH). The bicyclic ketone was present in the gas phase before nucleation in almost all experiments and has a (modelled and measured) temporal profile that grows with SOA mass (see Wyche et al., 2009). Furthermore, a higher gas phase yield was obtained for the bicyclic ketone under low NOx conditions which was matched by an ultimately higher aerosol yield. This hypothesis is also in agreement with the modelling studies of Johnson et al. (2005) who proposed significant partitioning of the O2-bridged ketone to the aerosol phase in their gas-aerosol coupled box model.

Finally, it is worth noting that latter-day laboratory and modelling studies have also shown that, despite their high volatility, reactive uptake of α,β-unsaturated-dicarbonyls (such as glyoxal and methyl glyoxal) by aerosols followed by aceration reactions, are a significant source of SOA (e.g. Healy et al., 2008; Hallquist et al., 2009). Kalberer et al. (2004) have shown that oligomerization reactions take place within the aerosol particles formed in the chamber photo-oxidation of TMB, resulting in oligomer molecules with masses of up to 900 Da. Kalberer et al. proposed that the oligomers observed could be formed via an acetal polymerization mechanism, with methyl glyoxal as the main monomer unit.

5. Conclusions

In the work presented, a detailed chamber specific photochemical box model, incorporating the MCMv3.1 degradation mechanism for 1,3,5-trimethylbenzene, has been used to simulate data measured during a series of chamber experiments in order to evaluate the mechanism under a variety of conditions. More specifically, the model was used in the interpretation of detailed measurements of organic gaseous oxidation products from a Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer (CIR-TOF-MS). Model-measurement comparisons have been used to gain an insight into the complex array of oxidation products formed, including the peroxy bicyclic ring opening products (e.g. α,β-unsaturated-γ-dicarbonyls and furanones) and relatively high molecular weight, multi-functional compounds, identified as O2-bridged peroxy bicyclic ring-retaining products (ketone and nitrate) in MCMv3.1. To our knowledge this is the first time such high mass, relatively stable species have been observed in the gas-phase and hence these findings will go some way to addressing current issues regarding ‘missing mass’ in the carbon balance of aromatic photo-oxidation systems. Good correlations observed between the temporal evolutions of measured and modelled products, formed at various stages of the oxidation process, give us confidence that the MCMv3.1 TMB mechanism does a reasonably good job of simulating the gas-phase degradation of TMB in the troposphere and supports the current general understanding of the gas-phase oxidation mechanisms of aromatics.

The model was also used to give insight into which gas-phase species were participating in SOA formation, with the primary and secondary peroxides (formed primarily under low NOx conditions), identified as potential candidates involved in the initiation of the SOA nucleation process. It has also been shown that the O2-bridged peroxy bicyclic ring-retaining nitrate and ketone products, and the primary ring opening products such as 3-methyl maleic anhydride, 2-methyl-4-oxo-2-pentenal and 3,5-dimethyl-5(2H)-2-furanone can also contribute to the formation and growth of TMB-SOA (possibly after further oxidative processing). The fact that the temporal evolution and formation yields of these products are distinctly different between high and low NOx conditions could explain the enhanced SOA yield observed under low NOx conditions, particularly when supported by evidence of their appearance in the chamber prior to nucleation in each experiment.

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