

Emissions and photochemistry of oxygenated VOCs in urban plumes in the Northeastern United States

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Abstract. Photochemical processes inside urban plumes in the Northeast of the United States have been studied using a highly detailed chemical model, based upon the Master Chemical Mechanism (MCM). The model results have been compared to measurements of oxygenated VOCs (acetone, methyl ethyl ketone, acetaldehyde, acetic acid and methanol) obtained during several flights of the NOAA WP-3D aircraft, which sampled plumes from the New York City area during the ICARTT campaign in 2004. The agreement between the model and the measurements was within 40–60 % for all species, except acetic acid.

The model results have been used to study the formation and photochemical evolution of acetone, methyl ethyl ketone and acetaldehyde. Under the conditions encountered during the ICARTT campaign, acetone is produced from the oxidation of propane (24–28 %) and i-propanol (<15 %) and from a number of products of i-pentane oxidation. Methyl ethyl ketone (MEK) is mostly produced from the oxidation of n-butane (20–30 %) and 3-methylpentane (<40 %). Acetaldehyde is formed from several precursors, mostly small alkenes, >C5 alkanes, propanal and MEK. Ethane and ethanol oxidation account, respectively, for 6–23 % and 5–25 % of acetaldehyde photochemical formation. The results highlight the importance of alkanes for the photochemical production of ketones and the role of hydroperoxides in sustaining their formation far from the emission sources.

1 Introduction

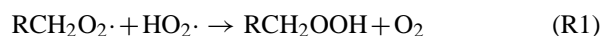
Oxygenated Volatile Organic Compounds (VOCs) are important products of the photo-oxidation of hydrocarbons and other organic species in the atmosphere. Oxygenated VOCs include carbonyls (aldehydes and ketones), alcohols and carboxylic acids. It has been known for many years that these classes of compounds are ubiquitous in the atmosphere (Singh et al., 1994, 1995, 2000, 2001, 2004; Colomb et al., 2006; Müller et al., 2006) and may account for a large fraction of the organic carbon in the troposphere, with some studies suggesting that they might be 2 to 5 times more abundant than all the non-methane hydrocarbons combined (Singh et al., 2001, 2004). Some of these species have been shown to have a large impact on ozone formation and chemistry. Acetone, for example, is an important source of HO_x radicals in the higher troposphere, where water concentration is low (Singh et al., 1995; McKeen et al., 1997; Jaeglé et al., 2001; Olson et al., 2004), and provides an important route to sequester active nitrogen in the form of peroxy acetyl nitrate (Singh et al., 1994, 1995; McKeen et al., 1997). In the lower atmosphere, carbonyls have been shown to be major radical sources, e.g. in winter-time polluted conditions (Emmerson et al., 2005) and in clean marine environments (Goldan et al., 2004; Sommariva et al., 2006; Madronich, 2006). More recently, oxygenated VOCs with multiple functional groups and low vapour pressure have been found to be important components of secondary organic aerosol both in laboratory and in field studies (Barsanti and Pankow, 2004; Hamilton et al., 2004; Odabasi and Seyfioglu, 2005; de Gouw et al., 2005; Madronich, 2006; Tong et al., 2006; Zhang et al.,



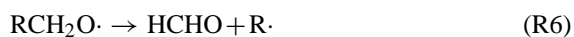
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2007). Despite their relevance for many atmospheric processes, there are still many uncertainties and gaps in our understanding of the sources, sinks and chemistry of oxygenated compounds (Jacob et al., 2002; Singh et al., 2004), due to the large variety of different oxygenated VOCs encountered and to the difficulty of measuring them (Northway et al., 2004).

In addition to direct emissions, oxygenated VOCs are photochemically formed from the reactions of peroxy and alkoxy radicals (RO_2 and RO , where R is a carbon chain) (Atkinson and Arey, 2003). The reactions between an organic peroxy radical and HO_2 at low NO_x (Reactions R1, R2) can result in the formation of a hydroperoxide (and a carboxylic acid in the case of an acyl peroxy radical) or a carbonyl. The reaction between two peroxy radicals at low NO_x forms either two alkoxy radicals (Reaction R3) or a carbonyl and an alcohol (Reaction R4):



Alkoxy radicals, which are formed by the reaction of an organic peroxy radical either with NO or with another peroxy radical (Reaction R3), are also known to form oxygenated hydrocarbons (Atkinson and Arey, 2003). Alkoxy radicals can react with O_2 to form a carbonyl (Reaction R5) or decompose to form a carbonyl and an alkyl radical (Reaction R6). Reaction with O_2 requires an hydrogen available on the radical carbon, so this path is not possible for tertiary alkoxy radicals (Atkinson and Arey, 2003). Depending on their molecular structure, some alkoxy radicals can also isomerize via a 1,5 H atom shift to form an hydroxy alkyl radical (Reaction R7) which, upon reaction with O_2 , will form an hydroxy peroxy radical:



The carbonyls formed in Reactions (R2), (R4), (R5) and (R6) are aldehydes, because their precursors are primary peroxy radicals; if the precursors are secondary or tertiary peroxy radicals, the carbonyl products will be ketones. Carbonyls, alcohols, hydroperoxides and carboxylic acids react with OH and with NO_3 . Some of these species, notably aldehydes and ketones, also photolyze. The products of these reactions are inorganic radicals and/or oxygenated peroxy radicals. Oxygenated peroxy radicals react further to produce multi-functional (alcohol + carbonyl) oxygenated compounds (Atkinson and Arey, 2003).

In the troposphere, the lifetime of oxygenates varies from a few hours (HCHO , CH_3CHO) to several days (CH_3OH) to a few months (acetone). At sea-level, the lifetime of acetone with respect to OH (τ_{OH}) is 64 days and with respect to photolysis (τ_{hv}) is 93 days, while for methyl ethyl ketone the two processes are approximately equal (12–13 days) (Baeza-Romero et al., 2005). Since they are both relatively long-lived species, they can be transported and act as radical sources initiating or enhancing photo-oxidation of other VOCs in remote regions and in the upper troposphere (McKee et al., 1997; Wennberg et al., 1998).

Photochemical formation is not the only source of oxygenated VOCs. Anthropogenic and biogenic emissions, biomass burning, plant decay, dry and wet deposition also play an important role in the budget of oxygenates and are as important or more important than photochemistry (Jacob et al., 2002; Singh et al., 2004). For example, biogenic emissions are sources of methanol 3–5 times stronger than hydrocarbons oxidation, but the two processes are comparable for acetone and acetaldehyde (Singh et al., 2004). In urban areas, primary emissions are more important than photochemical production for some carbonyls, such as acetone, methyl ethyl ketone, methanol and ethanol (de Gouw et al., 2005). Much uncertainty lies in the role played by oceans. For example, several studies suggest that the ocean is a net sink for methanol (Carpenter et al., 2004; Singh et al., 2004; Lewis et al., 2005), but it is more uncertain whether the ocean is a net sink (Warneke and de Gouw, 2001; Jacob et al., 2002; Marandino et al., 2005) or a net source (Singh et al., 2004) for acetone.

Typically, chemical mechanisms do not treat in much detail the various formation pathways of secondary organic compounds, leading to the underestimation of their concentrations, with possible consequences on the estimates of ozone production chemistry in remote regions. In this work, a fully explicit chemical model was used to clarify the photochemistry of a number of oxygenated VOCs and, in particular, of the two most abundant ketones (acetone and methyl ethyl ketone) and of acetaldehyde.

This study refers to conditions encountered during the New England Air Quality Study (NEAQS) 2002 and the International Consortium for Atmospheric Research on Transport and Transformation 2004 field campaigns (ICARTT, Fehsenfeld et al., 2006), but the conclusions can be generalized to other similar urban environments. The model, the measurements and the conditions are described in Sect. 2 and the results are shown in Sect. 3. The carbonyls formation processes are analyzed in Sect. 4. During the discussion, some species will be indicated in the text with their MCM codenames (in italics), for simplicity. The corresponding chemical structures are shown in the diagrams of Sect. 4. A companion paper (Sommariva et al., 2008) contains a similar study for alkyl nitrates.

Table 1. Initial values of model parameters (CH₄, CO, NO_x and O₃ in ppbv, VOCs in pptv, temperature in K, pressure in Pa).

| Parameter | Initial Value | Parameter | Initial Value |
|--------------------|---------------|--------------------------|---------------|
| CH ₄ | 1800 | acetylene | 837.1 |
| CO | 332.5 | benzene | 143.6 |
| NO _x | 34.9 | toluene | 609.8 |
| O ₃ | 90.0 | o-xylene | 106.7 |
| ethane | 2701.1 | m-xylene | 134.7 |
| propane | 1798.2 | p-xylene | 134.7 |
| n-butane | 392.5 | ethylbenzene | 73.1 |
| i-butane | 235.4 | n-propylbenzene | 18.8 |
| n-pentane | 359.9 | i-propylbenzene | 5.7 |
| i-pentane | 928.1 | 1,2,3-trimethylbenzene | 15.9 |
| n-hexane | 249.2 | 1,2,4-trimethylbenzene | 81.3 |
| 2-methylpentane | 257.2 | 1,3,5-trimethylbenzene | 21.1 |
| 3-methylpentane | 296.7 | 1-ethyl-2-methyl benzene | 23.4 |
| 2,2-dimethylbutane | 28.0 | 1-ethyl-3-methyl benzene | 40.5 |
| 2,3-dimethylbutane | 61.7 | 1-ethyl-4-methyl benzene | 40.5 |
| n-heptane | 92.5 | styrene | 5.9 |
| 2-methylhexane | 89.6 | dichloromethane | 84.9 |
| 3-methylhexane | 107.0 | chloroform | 2.6 |
| n-octane | 45.7 | 1,1,1-trichloroethane | 44.4 |
| n-decane | 23.3 | tetrachloroethene | 19.3 |
| cyclohexane | 66.3 | methyl t-butyl ether | 560.4 |
| ethylene | 1061.4 | formaldehyde | 1389.7 |
| propylene | 317.0 | acetaldehyde | 694.8 |
| 1-butene | 32.4 | propanal | 200.9 |
| c-2-butene | 13.7 | n-butanal | 46.6 |
| t-2-butene | 12.3 | n-pentanal | 18.5 |
| 1-pentene | 26.0 | methanol | 1925.4 |
| c-2-pentene | 11.5 | ethanol | 803.7 |
| t-2-pentene | 22.6 | i-propanol | 161.9 |
| 2-methyl-1-butene | 58.2 | acetone | 1004.6 |
| 3-methyl-1-butene | 13.5 | methyl ethyl ketone | 217.7 |
| α-pinene | 22.1 | dimethyl sulphide | 12.5 |
| β-pinene | 13.5 | temperature | 286.5 |
| isoprene | 1740.5 | pressure | 84 297 |

2 The model and the measurements

2.1 MCM model

The model used in this work is similar to the ones used by Neuman et al. (2006); Roberts et al. (2007) and has been described in detail in Sommariva et al. (2008). It was built using a subset of version 3.1 of the Master Chemical Mechanism (MCM, <http://mcm.leeds.ac.uk/MCMv3.1/>). The MCM is one of the most detailed chemical mechanisms for tropospheric chemistry available (Jenkin et al., 1997; Saunders et al., 2003; Jenkin et al., 2003) and, therefore, it is very suitable to study the degradation and the formation of pollutants in the lower atmosphere.

The subset includes the oxidation mechanisms of 64 VOCs (including 14 oxygenated VOCs) plus CH₄, CO and a complete inorganic mechanism taken from the 2003 IU-

PAC recommendation (Atkinson et al. (2003), http://www.iupac-kinetic.ch.cam.ac.uk/past_summary.html). The photolysis rates are calculated using the MCM parametrization (Saunders et al., 2003) for the end of July 2004 at the latitude and longitude of Boston (MA).

The model contains gas-phase chemistry only and no deposition to the surface or uptake of gas-phase species on aerosol. This is justified by the findings of previous field campaigns in the same area. During the NARE campaign, Daum et al. (1996) showed the formation of hydroperoxides (H₂O₂) in photochemically aged plumes from the Eastern coast of the United States and Canada and found that these plumes were mostly contained in layers isolated from the surface by a low altitude temperature inversion; Neuman et al. (2006) showed that, during NEAQS 2004, nitric acid (HNO₃) was conserved in urban plumes decoupled from the marine boundary layer during the transport from New England to

the ocean. Dilution is also neglected in the model, which does not matter if we are looking only at the chemical formation and evolution of certain species. The diluting effect can be taken into account when comparing the model results with the measurements (Sect. 3) by looking at enhancement ratios of the species of interest versus CO. The enhancement ratio is defined here as the ratio of the enhancements in two species relative to their respective background values. While dilution typically decreases the mixing ratios with time, the enhancement ratios are less sensitive to dilution. This approach to separate the effects of chemistry from those of mixing has some limitations (McKeen and Liu, 1993; McKeen et al., 1996; Parrish et al., 2007), but it does provide a useful tool for data analysis (de Gouw et al., 2005, 2008).

2.2 Conditions

The model is initialized using measurements obtained during the NEAQS 2002 campaign (de Gouw et al., 2005) and the ICARTT campaign in 2004 (Fehsenfeld et al., 2006). The initial concentration of NO_x is derived from the study by Neuman et al. (2006) and the initial concentrations of VOCs are derived from the emission ratios determined by de Gouw et al. (2005); Warneke et al. (2007). The details of the procedure used to calculate the emission ratios are explained in Sect. 2.3. The initial concentration of CO is set to a typical value measured in the Boston area during ICARTT, using an acetylene/CO ratio of $3.6 \text{ pptv ppbv}^{-1}$ (Warneke et al., 2007) with an estimated background [CO] of 100 ppbv. The initial concentrations of CH_4 and O_3 are estimated to be 1800 ppbv and 90 ppbv, respectively.

The initial concentrations of the species included in the MCM model are shown in Table 1 (see also Sommariva et al., 2008). The model is run for 5 days to simulate the evolution of the chemical composition of a typical urban plume. The model results (Sect. 3) are then compared with measurements of oxygenated VOCs obtained on board the NOAA research aircraft WP-3D during the ICARTT campaign.

The model results are shown in Fig. 1. The calculated concentrations of radicals (OH, HO_2 , NO_3) vary diurnally and show a general increase with time. The increase in $[\text{HO}_x]$ is driven by the build-up of ozone concentration during the 5 days, as well as the decrease of HO_x loss terms (NO_x and VOCs). The model also shows the comparatively fast removal of NO and NO_2 and the consequent formation of HNO_3 via the reaction of NO_2 with OH, in accord with the findings by Neuman et al. (2006). After the second day, $[\text{NO}_x]$ decreases below 1 ppbv. The concentration of NO_2 after the second day is however enough to form NO_3 via the reaction with increasingly high O_3 , which allows the continuation of night-time processing of VOCs during the following nights.

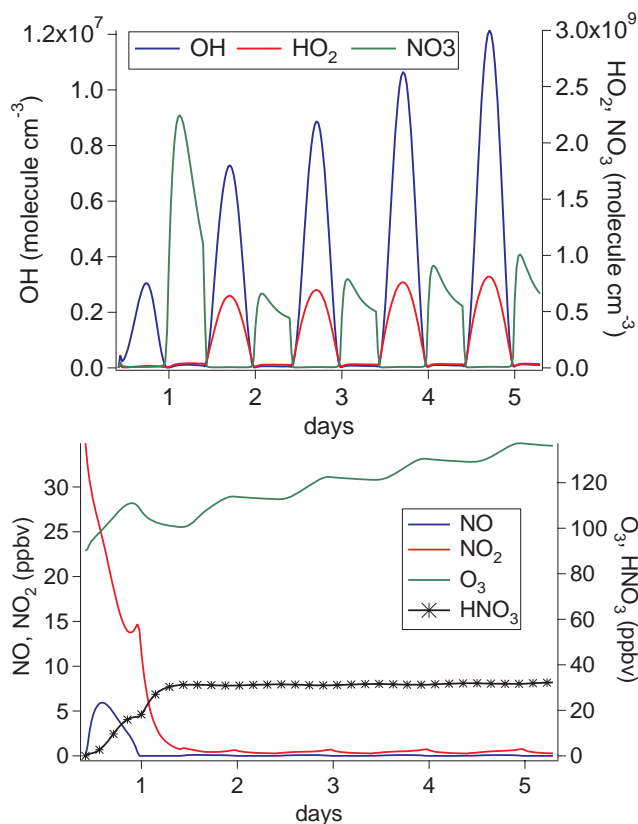


Fig. 1. Modelled concentrations of radicals (a), O_3 , NO_x and HNO_3 (b).

2.3 NEAQS parametrization

In a previous paper, de Gouw et al. (2005) derived the time evolution of VOCs and organic aerosol in air masses along the coast of New England by describing the measured data with a semi-empirical parametrization that includes (1) urban emissions of VOCs and the removal of those VOCs by OH, (2) secondary formation and removal of oxygenated species, (3) a biogenic term parameterized by measured isoprene and its photo-oxidation products and (4) a background concentration. The measurements were obtained during the NEAQS 2002 campaign (July–August 2002) onboard the NOAA research vessel *Ronald H. Brown*, downwind from the Boston and New York metropolitan areas.

The time evolution of VOCs in a typical urban plume can be calculated using Eq. (5) and the numbers in Table 1 of de Gouw et al. (2005), assuming that the biogenic term is negligible directly inside the plume, i.e. omitting the third term in Eq. (5). The results for acetone, methyl ethyl ketone (MEK), acetaldehyde, acetic acid and methanol are presented in Fig. 2, which shows the enhancement ratios of these species versus CO as a function of the photochemical age. The latter was calculated from measured

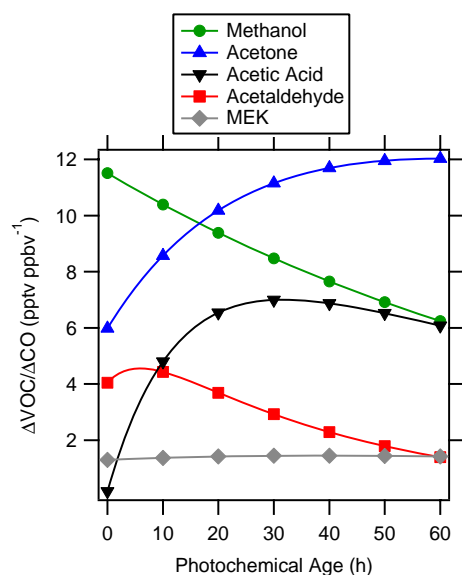


Fig. 2. Time evolution of oxygenated VOCs in a typical urban plume according to de Gouw et al. (2005). Curves are calculated using Eq. (5) and the numbers in Table 1 of de Gouw et al. (2005).

benzene/toluene ratios and a constant OH concentration of 3×10^6 molecule cm^{-3} , which explains why there is no diurnal variation in the removal and formation of the species in Fig. 2.

In de Gouw et al. (2005), VOC enhancement ratios were given with respect to acetylene; those have been converted here into enhancement ratios versus CO as described in de Gouw et al. (2008). The acetylene/CO emission ratios are different in de Gouw et al. (2005) (4.94 pptv ppbv⁻¹) and in Warneke et al. (2007) (3.6 pptv ppbv⁻¹), thus introducing an uncertainty in the conversion, which will be further discussed below. In the present paper (Sect. 3), we have compared the curves shown in Fig. 2 to the data from ICARTT and to the MCM model results. The implicit assumption in this comparison is that the photochemical age in Fig. 2 is in fact equal to the processing time in the model and of the sampled air masses. The average OH concentration of 3×10^6 molecule cm^{-3} , which was used to calculate the photochemical age in de Gouw et al. (2005), has an uncertainty of about a factor of 2, which will also be taken into account in the comparison.

While we have ignored the biogenic source of oxygenated VOCs in calculating the curves shown in Fig. 2, the model includes isoprene – as well as monoterpenes – because these species are typically present in urban areas. Based on the initial isoprene concentration in Table 1, and on the oxygenates-to-isoprene ratios in (de Gouw et al., 2005) (Table 1 in that paper), we estimate the biogenic contributions to oxygenated VOCs to be ~ 800 pptv for methanol, ~ 100 pptv for acetaldehyde, ~ 400 pptv for acetone, ~ 50 pptv for MEK and ~ 300 pptv for acetic acid. For methanol, acetaldehyde, ace-

tone and MEK, these values are smaller but not negligible compared to the initial conditions in Table 1. For acetic acid, this contribution is larger, as acetic acid is assumed to have zero anthropogenic emissions, but as shown below, ~ 300 pptv is significantly lower than the acetic acid observed in aged plumes.

2.4 Measurements

Oxygenated VOCs were measured during ICARTT using a Proton Transfer Reaction Mass Spectrometer (PTR-MS) on-board the NOAA WP-3D aircraft (de Gouw et al., 2006; de Gouw and Warneke, 2007). In this study, we use the data for acetone, methyl ethyl ketone (MEK), acetaldehyde, acetic acid, methanol, benzene and toluene, which were sampled for 1 s each every 17 s. The detection limit of the instrument is estimated from the 2σ noise in the background measurements and varied between 30 pptv for aromatic species to 300 pptv for methanol, depending on ion count rates and system backgrounds as described by de Gouw and Warneke (2007). The calibration accuracy of the measurements is estimated to be 15 % for most species and 50 % for acetic acid.

The other VOCs (alkanes, alkenes, acetylene, aromatics, dimethyl sulphide, methyl t-butyl ether, halogenated hydrocarbons) were measured by Gas Chromatography coupled to a Mass Spectrometer detector (GC-MS) after collection in stainless steel canisters (Schaufler et al., 1999; Reeves et al., 2007). A description of the other instruments on board the WP-3D can be found in Fehsenfeld et al. (2006); Neuman et al. (2006).

3 Results

During the ICARTT campaign the NOAA WP-3D aircraft sampled the outflow from New York City during multiple flights, at different times of the day and at various distances from the sources. In this study, we have used the data from six different flights. Figure 3 shows the portions of the flights during which the outflow from New York City was sampled. The flight tracks are color-coded by the measured mixing ratio of CO, which varied between 200 and 400 ppbv in the plumes. On 7 August, a flight was started in the evening hours, which sampled the outflow from New York City at a time of minimal processing by OH. On, 20 and 25 July, the NOAA WP-3D flew shortly downwind from New York City during the day. The outflow from New York City after one day of processing was sampled over the Atlantic Ocean on 21 July and 14 August, and after two days of processing on 22 July near Nova Scotia. The FLEXPART footprint analysis of these plumes (Stohl et al., 2003) indicated that most of the sampled emissions were from New York City. To further illustrate this point, Fig. 3 contains back trajectories for the three flights furthest away from New York City. In each case,

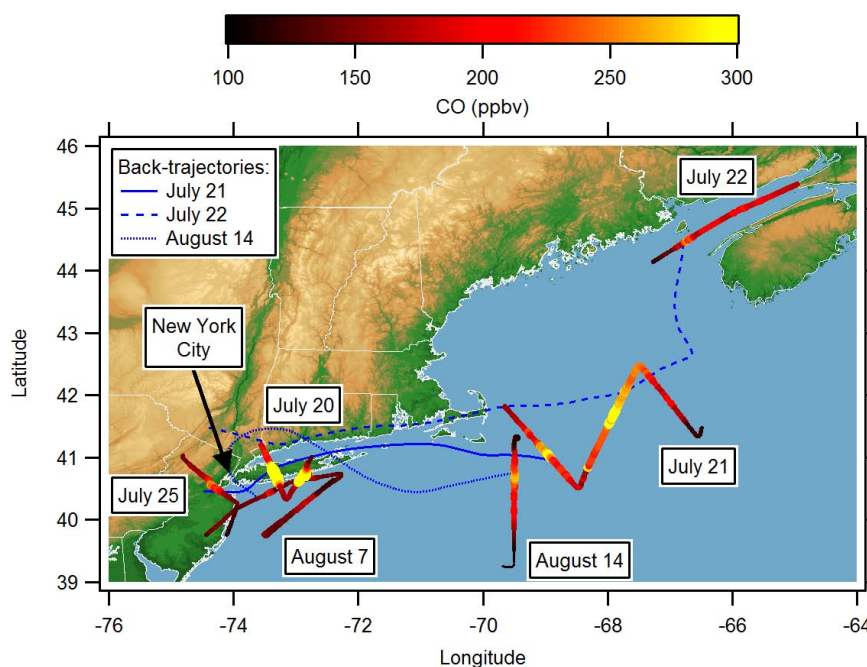


Fig. 3. Portions of the flight tracks from the NOAA WP-3D aircraft on six different days, during which the outflow from New York City was sampled. Back trajectories for three of the sampled plumes are also shown.

the back trajectory traces back to New York City within a few tens of kilometers.

In each sampled plume, the oxygenated VOCs as well as benzene and toluene were typically well correlated with CO, which is used here as an inert tracer for urban emissions. Examples are shown in Fig. 4, which contrasts the observations at night (7 August) with those after one day of processing (21 July). Assuming that urban emissions were roughly the same as during the day-time flights, the nighttime observations of the 7 August flight can be considered as representative of unprocessed air, even though aged plumes were occasionally sampled during the flight. The enhancement ratios, $\Delta\text{VOC}/\Delta\text{CO}$, are determined from the slopes of linear regressions to the data. Figure 4 shows marked differences between the enhancement ratios determined from the two flights. Toluene, which has a lifetime of 1–2 days, has a much higher enhancement ratio at night on 7 August than after 1 day of processing on 21 July. For several oxygenated VOCs (acetone, MEK and acetaldehyde) the opposite is observed: their enhancement ratios are significantly lower at night. Methanol and benzene are relatively inert and show similar enhancement ratios on both flights. Methanol and acetic acid typically show the lowest degree of correlation with CO, possibly caused by the importance of biogenic sources of these species that are, of course, not correlated with the urban emissions (see Sect. 2.3 and de Gouw et al., 2005). Despite a lower correlation, acetic acid typically shows lower enhancement ratios in unprocessed air masses as also seen in Fig. 4. While we cannot rule out that the dif-

ferences between the day-time and night-time flights are due to differences in emissions, the more likely explanation is that these differences are related to chemical processing and they will be interpreted as such in this study.

Figure 5 summarizes the enhancement ratios from all six flights shown in Fig. 3. For the most straightforward comparison with the MCM model, the data are plotted as a function of the numbers of hours since sunrise on the day of emission. We take this time since sunrise rather than the atmospheric transport time to reflect the fact that when measuring inside an urban air shed during the day, the hydrocarbon mixture is always aged to a significant extent. The enhancement ratios obtained during the nighttime flight (7 August) are shown at zero hours and represented by the solid circles; the open circles represent the results from the daytime flights. For the inert species methanol and benzene, the data show a gradual decrease over the course of two days of processing. For the much more reactive toluene, the removal was much faster. For the two ketones, the data show a gradual increase for acetone and a rapid increase for MEK as a result of processing. The data show a rapid increase of acetaldehyde on the first day and then a gradual decrease with time. Finally, for acetic acid a gradual increase during the first day was observed.

The measurement data in Fig. 5 are overlaid with (1) the results from the MCM model (solid curves), and (2) the parametrization of VOCs versus photochemical age derived from data obtained during NEAQS 2002 (de Gouw et al., 2005) (grey area). A range of values is shown here rather than the curves in Fig. 2 to reflect the uncertainties in the

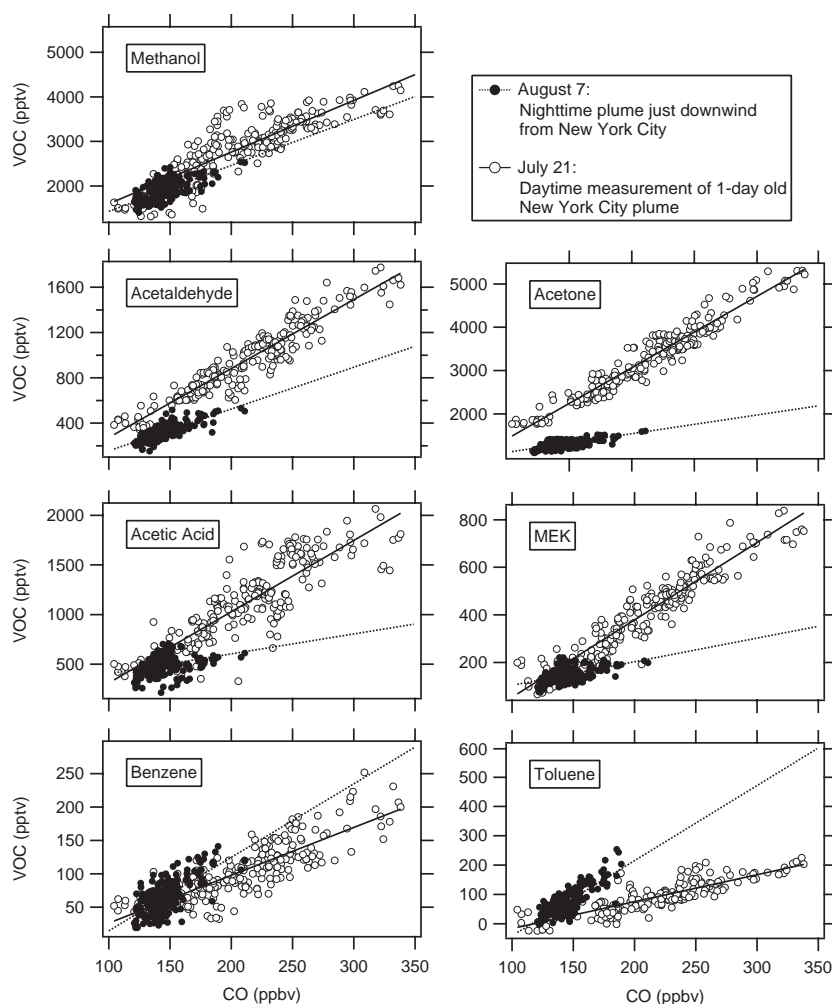


Fig. 4. Scatter plots of VOCs versus CO for the flights from 7 August, during which the outflow from New York City was sampled at night, and 21 July, after 1 day of processing.

acetylene/CO emission ratio and in the average OH concentrations as explained in Sect. 2.3. Because the NEAQS parametrization assumes a constant concentration of OH, the parametrization curves are smooth in time, whereas the MCM model shows different rates of oxidation at night and during the day. Also shown in Fig. 5 are the emission ratios according to Warneke et al. (2007). For methanol, acetaldehyde and benzene these ratios are somewhat lower than the initial values assumed in this work. Rather than actual differences in emissions, we believe these differences more likely reflect the uncertainties in determining emission ratios from a data set obtained outside an urban air shed. For acetone, acetic acid, MEK and toluene the emission ratios from (Warneke et al., 2007) agree quite well with the initial values in Table 1.

It is clear from Fig. 5 that the MCM model agrees well in an average sense with the NEAQS parametrization and the data from ICARTT, except for acetic acid, which is formed in

much larger quantities than is accounted for by the chemistry included in the MCM. Both the MCM model and the NEAQS parameterizations describe the trends in the ICARTT data for the other species reasonably well, although they underestimate the formation of acetaldehyde and MEK during the first day. This may be caused by the relatively low [OH] in the MCM model on the first day (Fig. 1). The agreement between the MCM model and the measurements is within 40–60 % for all the species, except acetic acid.

The acetic acid concentration calculated by the MCM model underestimates the measurements by a factor of 5 or more, although the NEAQS parametrization describes the measurements quite well (Fig. 5). In the MCM, acetic acid is formed in two ways: by reaction of the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ radical with RO_2 (HO_2 or another organic peroxy radical) and by ozonolysis of C3–C6 alkenes, forming the Criegee biradical $\text{CH}_3\text{CHOO}\cdot$ which then reacts with H_2O to form acetic acid. The former process can occur only when NO_x levels are

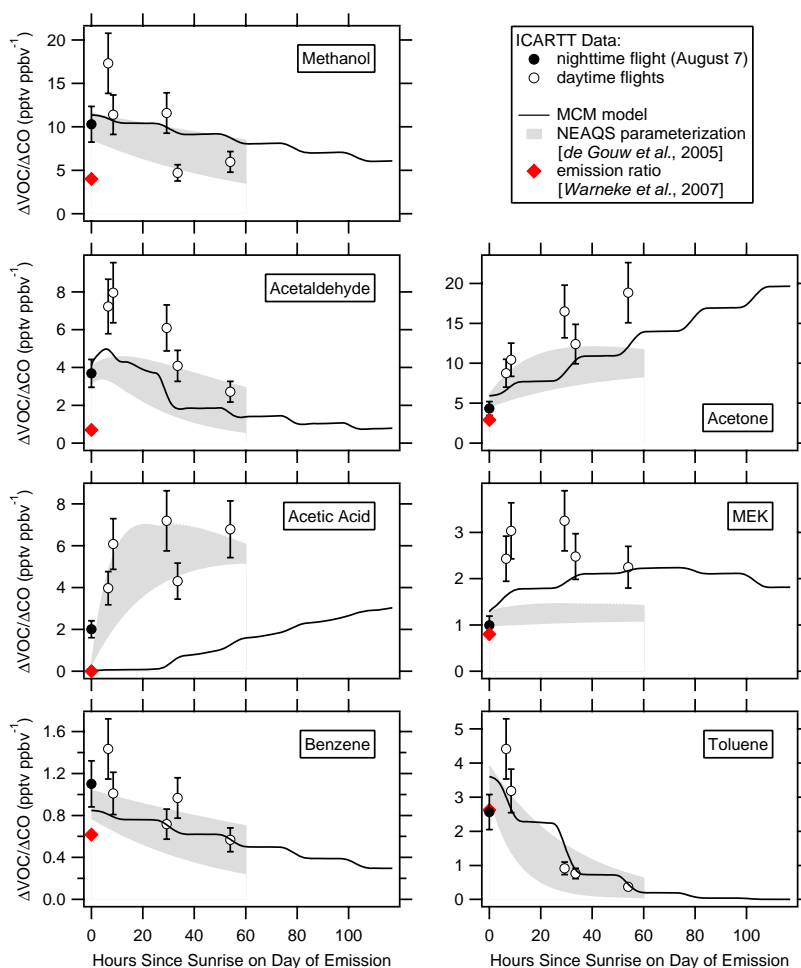


Fig. 5. Measured VOC enhancement ratios from six different flights downwind from New York City as a function of the transport time. Also shown are the calculation of the VOC enhancement ratios as a function of processing time using the MCM model (solid curve), the NEAQS parameterization (Fig. 2) of enhancement ratios as a function of photochemical age – with the grey area representing the range of possible values due to uncertainties in average OH and in the acetylene/CO emission ratio – and the emission ratio according to Warneke et al. (2007).

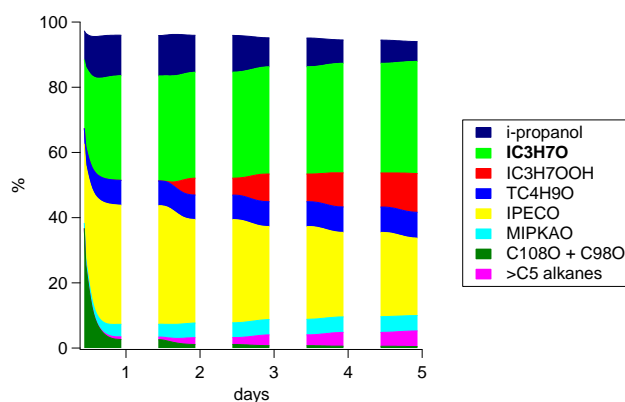


Fig. 6. Relative contribution of reaction pathways to the formation of acetone. See Fig. 7 for explanation of the MCM codenames.

sufficiently low (Fig. 1); the latter process is too slow to form significant amounts of acetic acid during the day, because alkenes are very reactive to OH and their concentrations decrease rapidly during the first day. Therefore, under the conditions used in this work, the MCM predicts significant formation of acetic acid only during the second day (Fig. 5). The rate coefficients for the formation (via $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{RO}_2$ routes) and destruction (via reaction with OH) reactions of acetic acid in the MCM are $\sim 40\%$ lower and $\sim 8\%$ higher, respectively, than the 2003 IUPAC recommendation (Atkinson et al., 2003). This cannot account for such a large discrepancy, especially during the first day. Direct formation of acetic acid following the addition of OH to acetone is not included in the MCM. However, laboratory studies (Turpin et al., 2006) indicate that the branching ratio for this reaction is small (< 0.05), which could not account for the observed discrepancy.

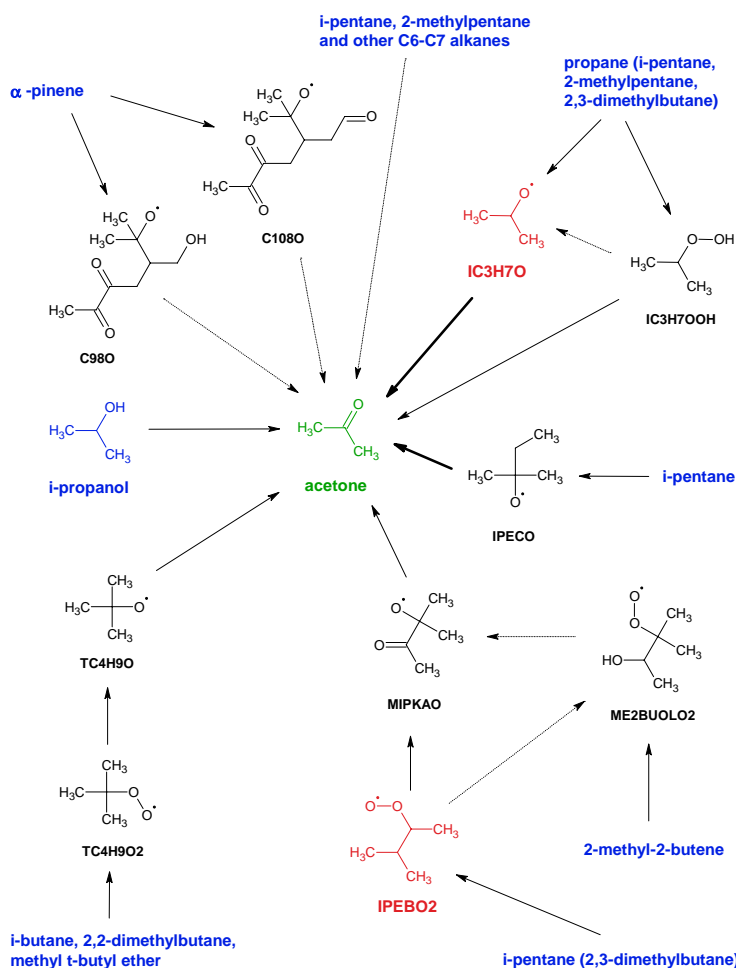


Fig. 7. Reaction scheme for the formation of acetone. Green indicates the target species, blue indicates the VOC precursors and red indicates an intermediate analyzed in detail in Sommariva et al. (2008).

The inability of chemical models to reproduce measured concentrations of acetic acid has been known for some time (e.g., Madronich et al., 1990; Jacob et al., 1992; Talbot et al., 1995; Ito et al., 2007). There is still considerable uncertainty in our understanding of acetic acid budget (Singh et al., 2000): biomass burning (Helas et al., 1992; Talbot et al., 1992, 1999; Yokelson et al., 1999; de Gouw et al., 2006; Ito et al., 2007) and biogenic emissions (Klemm et al., 1994; Talbot et al., 1995; Kesselmeier, 2001) have been proposed as major sources of acetic acid. However, it must be noted that the measurements shown in Fig. 5 were filtered to eliminate the biomass fire plumes and that the emission ratio for acetic acid is assumed to be zero in this work (de Gouw et al., 2005). This suggests that the discrepancy between the model and the measurements may be attributed either to missing direct emissions (likely biogenic) or to an unknown gas-phase or heterogeneous production mechanism (Nolte et al., 1997; Turpin et al., 2006).

4 Photochemical formation of ketones

The MCM contains a very detailed description of the oxidation processes of most of the known emitted VOCs (Jenkin et al., 1997; Saunders et al., 2003). The mechanism is by no means complete, but it reflects the current understanding of tropospheric chemical processes and allows to follow the formation and the degradation pathways of a species down to CO_2 and H_2O , taking into account all the known photochemical sources and sinks. In the following sections the formation pathways of acetone, methyl ethyl ketone (MEK) and acetaldehyde will be discussed in detail and their relative importance assessed.

4.1 Acetone

The photochemical formation of acetone involves a large number of routes, though only a few of them contribute by more than a few percent to the total production rate. The relative importance of each pathway does not change

significantly from day to day, with the exception of the first day, during which a significant contribution ($\sim 10\%$ on average) comes from the decomposition of α -pinene derived alkoxy radicals (Figs. 6 and 7).

The two major photochemical sources of acetone are the decomposition of the alkoxy radical *IPECO* and the reaction of the alkoxy radical *IC3H7O* with O_2 (Fig. 7). The former accounts for 30–35% and is a product of *i*-pentane oxidation, while the latter accounts for 35% on the first day down to 25% on the fifth day of the total acetone formation (Fig. 6). Sommariva et al. (2008) have analyzed the formation processes of the peroxy radical *IC3H7O2*, which is the only significant precursor of *IC3H7O*. A small fraction of this alkoxy radical is produced via photolysis of the hydroperoxide *IC3H7OOH*, which is formed starting from the second day when NO_x has been largely removed (Fig. 1). The hydroperoxide is, however, more likely to directly form acetone via reaction with OH (which is faster than photolysis) and contributes in this way to acetone formation for $<10\%$ (Fig. 6).

According to the analysis by Sommariva et al. (2008), who used the same model and the same initial conditions, about 80% of the peroxy radical *IC3H7O2* is produced via the reaction of propane with OH over the five days run of the model simulation. The rest comes from the oxidation of *i*-pentane, 2,3-dimethylbutane, 2-methylpentane and a number of higher ($>C_6$) hydrocarbons (Sommariva et al., 2008). From these numbers it can be estimated that about 24–28% of acetone is produced by the reaction of propane with OH.

The other two significant sources of acetone are the alkoxy radicals *TC4H9O*, which accounts for $\sim 10\%$ of the total acetone production, and *MIPKAO*, which accounts for $\sim 5\%$ of the total acetone production (Fig. 6). The former is a product of *i*-butane, 2,2-dimethylbutane and methyl *t*-butyl ether (MTBE), while the latter is a product of the oxidation of *i*-pentane and 2,3-dimethylbutane, with minor contributions from 2-methyl-2-butene (Fig. 7).

The analysis of the formation of the *IPEBO2* peroxy radical, which is the most important precursor of *MIPKAO*, discussed in Sommariva et al. (2008) indicates that the reaction between *i*-pentane and OH is the most important ($>90\%$) source of this alkoxy radical. It also indicates that it accounts for a significant fraction of the 20% of *IC3H7O2* not coming from propane reaction with OH. It can therefore be inferred that *i*-pentane is overall the most important precursor of acetone, followed by propane.

Acetone is also formed by reaction of *i*-propanol with OH. This pathway accounts for up to 15% of the total production, decreasing with time to about 6% as the concentration of *i*-propanol decreases (Fig. 6). The photochemical production of *i*-propanol occurs via a peroxy-peroxy reaction involving the *IC3H7O2* peroxy radical and it is significant only at low NO_x , i.e. starting from the second day. It is however very slow, because only 20% of the reaction of *IC3H7O2* with other peroxy radicals forms *i*-propanol. Therefore this source

of acetone is largely related to direct emissions of *i*-propanol (Table 1).

A small fraction ($<5\%$) of acetone is produced by a number of larger hydrocarbons, such as 2-methylpentane, 2-methylhexane, 2,2-dimethylbutane and other $>C_6$ alkanes and alkenes through a variety of other routes (Fig. 6).

The results of this analysis can be compared to those discussed in Lewis et al. (2005), who studied the formation processes of acetone, acetaldehyde and methanol using measurements taken at Mace Head, on the Western coast of Ireland, and a model based upon the MCM. According to their analysis, the main precursors of acetone are *i*-pentane, *i*-butane and propane, either directly or via the formation of stable hydroperoxides. The main difference with the results discussed in this work is the role of *i*-butane to which Lewis et al. (2005) attributed 27% of acetone formation on the first day and 22% on the fifth day (including the contribution by the hydroperoxide). As shown in Fig. 7, *i*-butane is the major precursor of the *TC4H9O* alkoxy radical, which, according to the analysis shown here only accounted for about $\sim 10\%$ of the total acetone formation (Fig. 6). On the other hand, Lewis et al. (2005) attributed only 6–13% to the reaction of propane with OH (compared to 24–28%) and 6–16% (compared to $<10\%$) to the reaction with the hydroperoxide *IC3H7OOH*. The role of *i*-pentane is more difficult to assess, due to the variety of routes. Lewis et al. (2005) calculated about a third (on day 1) to a fifth (on day 5) of acetone being produced via the *IPECO* pathway (Fig. 7) and another 3–8% via the *MIPKAO* pathway. These numbers compare well with those presented in this analysis (Fig. 6, though they neglect minor routes and the contribution of *i*-pentane to the formation of the *IC3H7O* radical (Sommariva et al., 2008).

In short, the analysis by Lewis et al. (2005) shows a larger contribution from *i*-butane and a smaller contribution from propane compared to this work, but the two analyses agree reasonably well as far as the other acetone formation routes are concerned. Both analyses highlight the role of hydroperoxides in sustaining the formation of acetone after depletion of NO_x and far from the emission points of the precursors. It must be noted that, while the modelling approach of this study and of that by Lewis et al. (2005) are very similar, the initial conditions used by the two models are different. In this work the initial concentrations of VOCs were derived from the observations, while Lewis et al. (2005) estimated theirs on the basis of the UK emission inventory. In particular, CO, O_3 , NO_x , propane and pentane were lower and butane was higher than the values used in this work (Table 1). The differences in the model initialization can largely explain the differences in the results.

Both our analysis and the one by Lewis et al. (2005) indicate a less important role of propane and a more important role of higher alkanes in the photochemical production of acetone compared to the calculations by Jacob et al. (2002). Using the GEOS-CHEM global model and the EDGAR emission inventory, Jacob et al. (2002) calculated

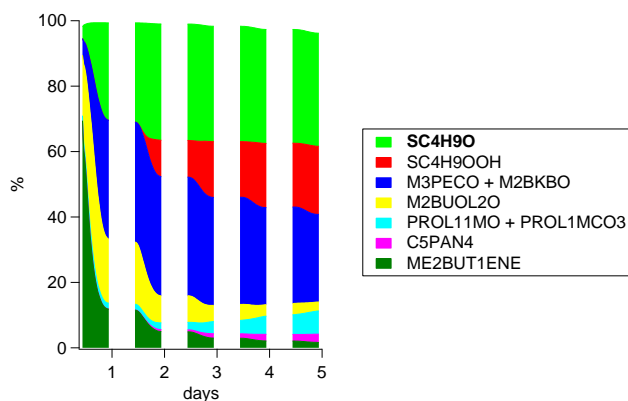


Fig. 8. Relative contribution of reaction pathways to the formation of MEK. See Fig. 9 for explanation of the MCM codenames.

that ~60 % of the photochemical production of acetone from alkanes is due to propane oxidation and about 30 % to butane and pentane oxidation. However, the chemical scheme used in GEOS-CHEM is not as detailed as the MCM.

It must also be noted that 2-methyl-3-buten-2-ol (MBO), which has been identified as an important acetone precursor (Fantechi et al., 1998; Alvarado et al., 1999; Singh et al., 2000; Jacob et al., 2002), was not measured during ICARTT and therefore could not be taken into account in this work.

4.2 MEK

Methyl ethyl ketone has a smaller number of precursors and formation pathways than acetone. Besides, while acetone precursors are mostly alkanes (Sect. 4.1), MEK is also formed from alkenes, particularly during the first two days. During the first day, direct oxidation of 2-methyl-1-butene accounts, on average, for 27 % of MEK formation, decreasing to less than 10 % on the second and less than 5 % on the remaining days (Fig. 8). The role of 2-methyl-1-butene is not limited to direct oxidation, because this species is a precursor (though not the only one) of several other intermediates of MEK formation (Fig. 9).

The alkoxy radical *M2BUOL2O*, for example, is produced from 2-methyl-1-butene during the first day, but from the *IPEAO2* peroxy radical from the second day onward (Fig. 9). The *M2BUOL2O* route accounts for up to 30 % on the first day decreasing with time down to only 3 % of MEK formation on the fifth day (Fig. 8).

The *IPEAO2* peroxy radical is mostly formed by the oxidation of *i*-pentane (<80 %) and 3-methylpentane (<20 %). Besides the *M2BUOL2O* alkoxy radical, it forms another peroxy radical (*BUT2CO3*), which is the precursor of a PAN-like compound (*C5PAN4*, Fig. 9), whose reaction with OH accounts for less than 3 % of MEK formation during the last three days (Fig. 8). Most of *BUT2CO3*, however, reacts to form another peroxy radical, *SC4H9O2* (Fig. 9). This is a key precursor of MEK, as the reaction of the corresponding

alkoxy radical (*SC4H9O*) with O_2 accounts for 20–35 % of the total MEK formation and, after the first day, the reaction of the corresponding hydroperoxide (*SC4H9OOH*) with OH accounts for another 10–20 % of the total MEK formation (Fig. 8).

According to the analysis discussed in Sommariva et al. (2008), who used the same model and initial conditions, the formation route of *SC4H9O2* via *BUT2CO3* is secondary and accounts only for 5 % or less. Most of *SC4H9O2* (85–95 %) is formed from the oxidation of *n*-butane. Using these values, it can be estimated that about 20–30 % of MEK is formed from the reaction of *n*-butane with OH.

The other major formation pathways of MEK go via two alkoxy radicals (*M3PECO* and *M2BKBO*), which come both from 3-methylpentane (Fig. 9). Together they account for about 10 % to 30 % on the first day and about 30–40 % on the following days of the total MEK formation (Fig. 8). The most important of the two is *M3PECO* (Fig. 9). *M2BKBO* becomes significant only after the third day due to its longer formation route, which involves a stable ketone (3-methyl-2-pentanone). The ratio of the contributions to MEK formation of these two alkoxy radicals (*M3PECO*:*M2BKBO*) is about 85:15 during the fourth and fifth days.

Another secondary route for the photochemical formation of MEK is the one via the alkoxy radical *PROL11MO* and, less importantly, the decomposition of the peroxy radical *PROL1MCO3* after reaction with NO. Via different pathways these two intermediates are both produced from the oxidation of 3-methylhexane and, to a lesser extent, 2-methyl-1-butene (Fig. 9). Together they account for at most 7 % of the total MEK formation (Fig. 8).

4.3 Acetaldehyde

Analysis of acetaldehyde photochemical formation is necessarily more qualitative due to the large number of formation pathways. In this section only the most important pathways will be discussed, neglecting those that contribute less than 5 % to the formation of acetaldehyde.

Approximately half (40–50 %) of acetaldehyde is formed via the reaction of the *C2H5O* alkoxy radical with oxygen (Fig. 10). The most important precursor of this alkoxy radical is the *C2H5O2* peroxy radical, whose formation has been described in detail in a previous paper (Sommariva et al., 2008). The corresponding hydroperoxide (*C2H5OOH*) begins forming on the second day, when the concentration of NO_x is low and contributes up to 15 % to the formation of acetaldehyde via reaction with OH.

According to the analysis by Sommariva et al. (2008) ethane is a major precursor of *C2H5O2* (15–45 %), together with propanal, MEK and a range of >*C5* alkanes. Therefore the formation of acetaldehyde can be attributed to the reaction of ethane with OH for about 6 % on the first day increasing to ~23 % on the fifth day. These values agree rather well with those reported by Lewis et al. (2005), though they

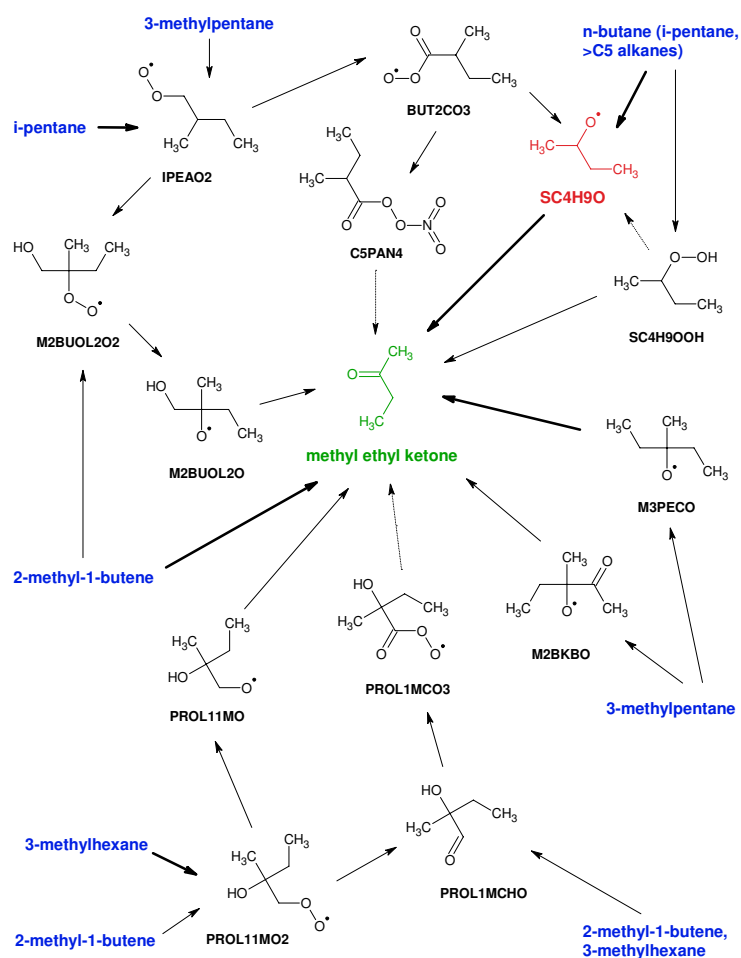


Fig. 9. Reaction scheme for the formation of MEK. Green indicates the target species, blue indicates the VOC precursors and red indicates an intermediate analyzed in detail in Sommariva et al. (2008).

estimated higher (9.5 %) contribution from ethane on the first day and slight lower (17.5 %) on the fifth day.

About 30 % of $C_2H_5O_2$ is formed from the $C_2H_5CO_3$ peroxy radical, which has a very large number of precursors (including propanal, see Sommariva et al., 2008) and which reacts with NO_2 to form PPN. The reaction of PPN with OH is a minor source of acetaldehyde accounting for 5–7 % of its total formation rate (Fig. 10).

Besides the formation of the $C_2H_5O_2$ peroxy radical, MEK contributes to the production of acetaldehyde also by forming most (50–60 %) of the $MEKBO$ alkoxy radical, via reaction with OH. The decomposition of the $MEKBO$ alkoxy radical is a relatively minor formation pathway for acetaldehyde, accounting for 4–7 % of its total formation rate (Fig. 10).

During the first day, propene and other alkenes significantly contribute to the formation of acetaldehyde. Propene accounted for about 9 %, butenes for about 7 % and pentenes for about 5 %. These numbers are in broad agreement with the results of Lewis et al. (2005), though somewhat higher

for propene and the pentenes. Propene is also the most important precursor of the *HYPROPO* alkoxy radical (Fig. 10), especially during the first two days when its contribution to acetaldehyde formation is most important (up to 25 %). The role of these species decreases very quickly, because of their high reactivity.

Finally, a significant contribution to the photochemical formation of acetaldehyde comes from the reaction of ethanol with OH (Fig. 10). This route accounts for 5 % up to 25 % of acetaldehyde formation, peaking on the second day, and it is mostly related to direct emissions of ethanol (Table 1), since its photochemical production is very slow. The role of ethanol emissions in acetaldehyde formation is particularly interesting in view of the possible increase in the use of ethanol as fuel in the next future. Jacobson (2007) estimated that, in a scenario where ethanol replaces gasoline, the increase in atmospheric concentrations of ethanol and acetaldehyde would be of 20 ppbv and 1.5 ppbv, respectively, with significant impact on ozone and PAN concentrations. Most of the increase in acetaldehyde concentration would be

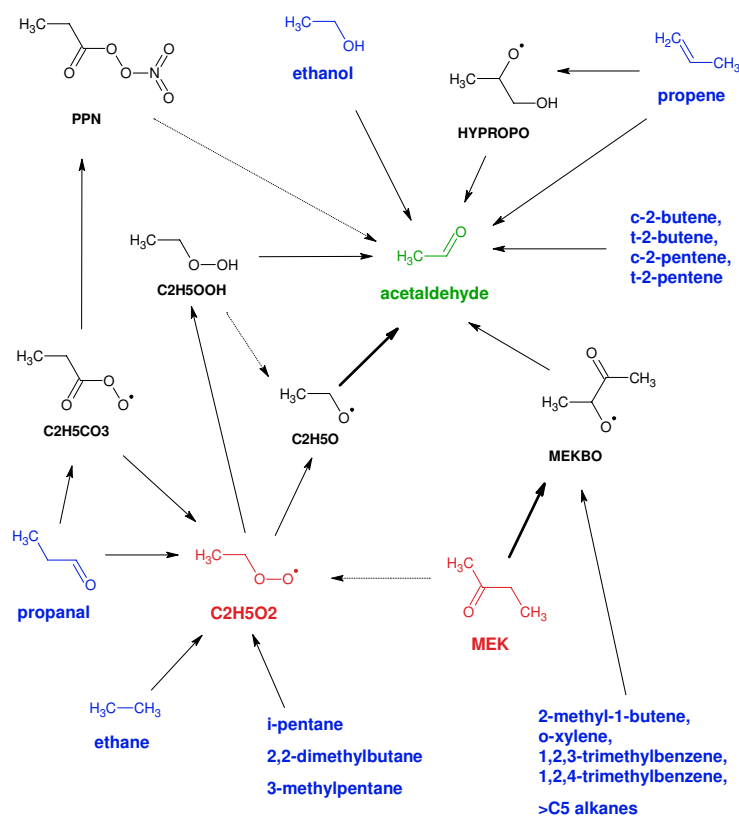


Fig. 10. Reaction scheme for the formation of acetaldehyde. Green indicates the target species, blue indicates the VOC precursors and red indicates an intermediate analyzed in detail in Sommariva et al. (2008).

related to photochemical production (up to three times more important than increased emissions) from unburnt ethanol (Jacobson, 2007). Considering that the initial concentration of ethanol in our model is about 800 pptv (Table 1), the increase predicted by Jacobson (2007) would make ethanol the single most important source of acetaldehyde, largely dominating all the other photochemical sources.

5 Conclusions

The photochemical evolution of urban plumes in the Northeast of the United States has been studied using a highly detailed chemical model based upon the Master Chemical Mechanism (MCM). The model has been initialized using measurements and VOC emission ratios from the NEAQS 2002 and ICARTT 2004 field campaigns. The model results have been compared to measurements of oxygenated VOCs taken during the ICARTT field campaign. With the exception of acetic acid, the model underestimates the measured concentrations of oxygenated VOCs by 40–60 %, but is able to reproduce their variation in time. The model also agrees very well with a simple empirical parametrization obtained from

the measurements taken during a previous field campaign in the same area.

Using the explicit description of the chemistry provided by the MCM, the photochemical formation and the evolution of the most important ketones (acetone and methyl ethyl ketone) has been determined quantitatively and the relative importance of their different formation pathways has been calculated. Approximately 24–28 % of acetone formation can be attributed to the reaction of propane with OH and about 20–30 % of MEK to the reaction of n-butane with OH. The most important precursor of acetone is i-pentane, via a number of different pathways, while emissions of i-propanol account for up to 15 % of the photochemical production of acetone. Besides n-butane, the most significant precursor of MEK is 3-methylpentane, which accounts for up to 40 % of its total production rate. At low $[\text{NO}_x]$, the hydroperoxides formed by the reactions of the peroxy radicals with HO_2 provide a significant (10–20 %) pathway to the formation of acetone and MEK, sustaining their photochemical production far away from the emission sources.

Acetaldehyde has a very large number of sources, which include propanal, MEK and a range of $>\text{C}_5$ alkanes and some aromatics. The reaction of ethane with OH accounts

for 6 % up to 23 % of acetaldehyde formation. During the first two days, alkenes (particularly propene) are also significant sources. Ethanol, which is mostly emitted, accounts for 5 % up to 25 % of acetaldehyde photochemical formation.

Clearly, these results are dependent on the initial conditions used by the model. Depending on the initial NO_x levels, the low NO_x formation pathways can become significant later and farther away from the emission sources. The values used in this work are based on measured emission ratios and should be fairly similar for other urban areas characterized by comparable industrial activity and mostly traffic-related emissions.

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