

Simulations of EUPHORE and field experiments using a master chemical mechanism

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Introduction

In recent years, a master chemical mechanism (MCM) has been developed to describe the atmospheric degradation of VOC in the atmosphere (Jenkin *et al.*, 1997a; Saunders *et al.*, 1997). The MCM has been developed as part of a collaborative project between the University of Leeds, AEA Technology plc and the UK Meteorological Office, and funded by the UK Department of the Environment (now the UK Department of the Environment, Transport and the Regions). The mechanism is near-explicit, and draws on the latest chemical kinetic and mechanistic results. The MCM has been validated for ozone production against the carbon bond mechanism (CBMIV), which in turn was validated against US smog chamber data (Derwent *et al.*, 1998). The latest version of the MCM treats the degradation of 123 VOC, and can be found on the internet at <http://www.chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html>. In this paper, we describe the evaluation of the MCM both through smog chamber and field experiments.

Smog chamber work

In order to test various aspects of a recently developed α -pinene mechanism, chamber experiments were carried out in the *EU*ropean *PHO*tochemical *RE*actor (EUPHORE) at Valencia. Two experimental systems were studied as followed: NO_x/ethene/toluene/*n*-butane and NO_x/ethene/toluene/*n*-butane/ α -pinene, the object being to investigate the effect on the final ozone concentration of the addition of α -pinene to the experimental system. The systems were then modelled using the MCM, with diurnally varying photolysis rates calculated for the latitude of Valencia, (39.5°N), and the appropriate day of the year using the UVFLUX model

(Hayman, 1997; Jenkin *et al.*, 1997b). The initial concentrations and conditions of the two experimental runs are summarised below in Table 1.

Table 1 - Summary of initial concentrations and conditions used in the EUPHORE chamber

	no α -pinene	with α -pinene
Start time	08:40	08:15
End time	16:29	16:05
Average temperature ($^{\circ}$ C)	24	25.1
Maximum temperature ($^{\circ}$ C)	26.5	27.3
Pressure (mbar)	1004	1001
Initial concentrations (ppb):		
[NO]	177	178
[NO ₂]	20	16
[C ₂ H ₄]	254	246
[n-C ₄ H ₁₀]	257	248
[toluene]	73	68
[α -pinene]	0	28

The results from the simulation are shown in Figures 1 and 2 (the smog chamber data are preliminary and have been provided by Dr. Lars Ruppert of the University of Wuppertal).

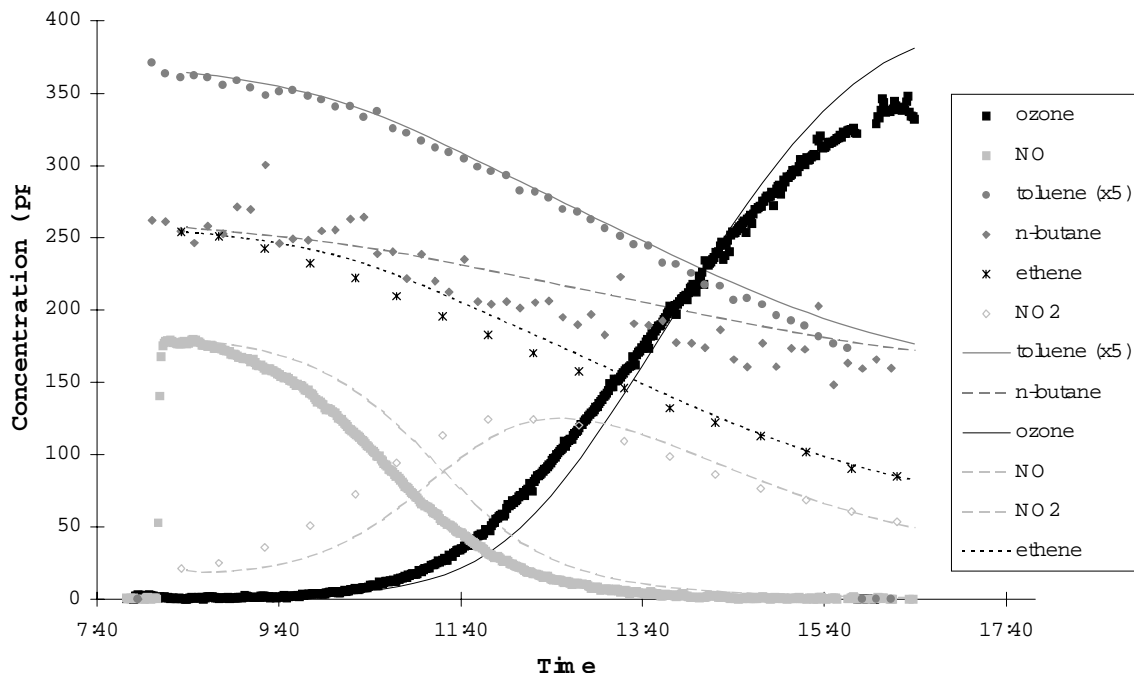


Figure 1 - Results from the simulation of the NO_x/ethene/toluene/*n*-butane system. The measurements are indicated by symbols and the MCM results by solid lines.

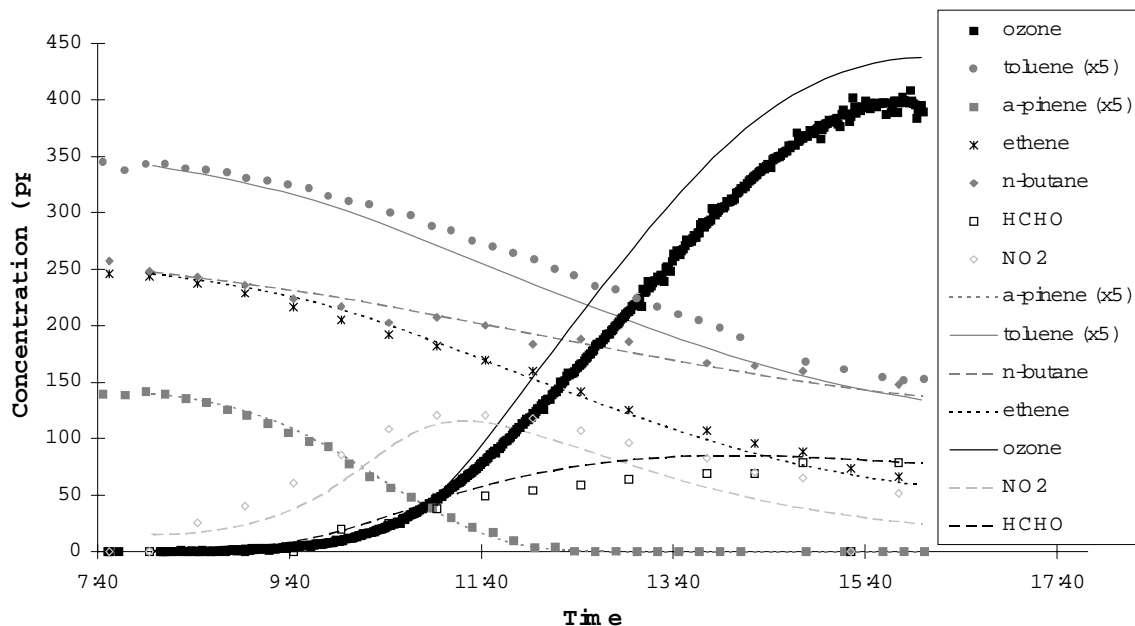


Figure 2 - results from the NO_x/ethene/toluene/*n*-butane/ α -pinene system. The measurements are indicated by symbols and the MCM results by solid lines. (Note that the NO profiles have been omitted in order to see clearly the α -pinene comparison)

The addition of 28 ppb of α -pinene to the system results in the production of an extra 50 ppb of ozone under these conditions. The MCM generally reproduces the observed concentrations of most of the components of the smog chamber systems.

Field work

Field campaigns have allowed the evaluation and testing of the MCM against field measurements. A comparison has been made between *in situ* measurements of radicals (OH, HO₂ and RO₂) and simulations using a constrained box model. The constraints are provided by measurements of the stable species, such as non-methane hydrocarbons (NMHC), CO, CH₄, NO_x and O₃. This approach depends on the short-lived nature of the radicals, which react quickly to changes in local ambient conditions (solar flux, concentration of NO_x and NMHC), but are not directly affected by atmospheric transport. It is, therefore, sufficient to use a zero-dimensional model to describe the fast chemical processes.

The model has been applied to field campaigns both at the Mace Head Atmospheric Research Station (*Eastern Atlantic Summer Experiment* 1996, 'EASE96' and the *Eastern Atlantic Spring Experiment* 1997, 'EASE97') near Galway, Ireland (53°19'34"N, 9°54'14"W) and the Cape Grim Baseline Air Pollution Station (40°41' S, 144°41' E) in Tasmania (Southern

Ocean Atmospheric Photochemistry EXperiment, 'SOAPEX'). Both sites are essentially clean air sites, though subject to pollution in certain wind directions. During the campaigns, OH and HO₂ were determined using the FAGE technique (Creasey *et al.*, 1997) and (HO₂+ΣRO₂) by use of a PERCA (peroxy radical chemical amplifier) instrument (Monks *et al.* 1998). Other salient measurements included the concentrations of NMHC, NO, NO₂, O₃, HCHO, CO, CH₄, H₂O, and PAN, as well as j(O¹D), j(NO₂), aerosol and meteorological data.

Measured concentrations of NMHC, CH₄ and CO were used to construct appropriate models for each campaign. The product of the concentration of each hydrocarbon (and CO) measured during each campaign and its rate coefficient for reaction with OH was calculated. Figure 3 shows the result of this calculation for several field campaigns that the Leeds group have participated in recently. Where appropriate, campaigns have been segregated into different air mass types. During the EASE campaigns, the air tended to be clean when from the Atlantic or tropical regions, but polluted when it had travelled in an anti-cyclonic direction taking in emissions from the UK or Europe. During the 1997 campaign, there was a short period where air arrived from polar regions. During the SOAPEX campaign, there were a few periods of baseline air when the air was very clean (NO_x < 50 ppt). The AEROBIC (AEROSol formation from BIogenic organic Carbon) campaign took place in a forested environment in northern Greece and the average OH losses due to CO, CH₄ and NMHC are included as they are very different to the other two locations.

As you move from left to right in figure 3, the air is becoming cleaner and cleaner, with the air masses encountered during the AEROBIC campaign containing most NO_x, and those in the SOAPEX campaign containing least. In the clean air masses, most OH reacts with CO and CH₄ (>95% in baseline air during SOAPEX cf. <15% during AEROBIC). During EASE96, around 95% of the OH loss due to CO and hydrocarbons could be accounted for by CO, CH₄, ethane, ethene, propane, propene, isoprene, *cis*- and *trans*-2-butene, toluene, 1,3-butadiene, and 1,3,5-trimethylbenzene. These species form the basis of the model, with the mechanisms taken from the MCM. Dry deposition and heterogeneous loss terms are also added.

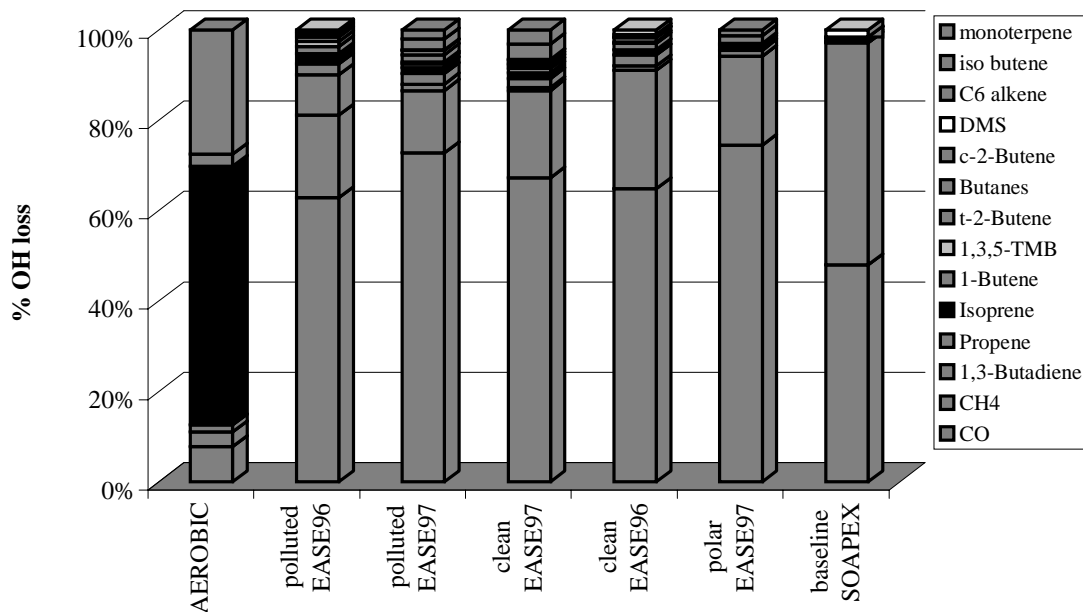


Figure 3 – Importance of hydrocarbons and CO for loss of OH during recent field campaigns

EASE96

The model/measurement comparisons have been discussed in detail before (Carslaw *et al.* 1999a) and the results are summarised in Table 2. August 3rd had low concentrations of NO_x and anthropogenic hydrocarbons, whereas July 17th and 18th were both characterised by higher NO_x and NMHC, and on July 17th, high concentrations of isoprene (~ 350 ppt maximum).

Table 2 – Comparison of measured and modelled radicals from EASE96 (concentrations in molecule cm⁻³)

Date	[OH]/10 ⁶		[HO ₂]/10 ⁸		Σ[HO ₂ +RO ₂]/10 ⁸	
	Measured	Modeled	Measured	Modeled	Measured	Modeled
July 17 th	--	--	2.61	2.96	2.55	3.98(3.37 [*])
July 18 th	--	--	1.12	2.02 (1.08 [†])	1.92	2.54 (1.86 [†])
August 3 rd	2.33 [‡]	3.28 [‡]	--	--	3.13	2.30

^{*}value obtained when isoprene peroxy radicals subtracted from model estimation of PERCA observations; [†]value obtained when γ(HO₂)=1; [‡] nonzero values only for [OH] (for more details see Carslaw *et al.*, 1999a).

Figure 4 shows a comparison between measured and modelled peroxy radicals on July 17th. An asymmetry about solar noon was observed in the measured peroxy radicals and model HO₂ and CH₃O₂ also peak after noon. Peroxy radicals formed during the initial oxidation of isoprene by OH (isoprene peroxy radicals) peak somewhat earlier (12:30), when the isoprene concentration is greatest.

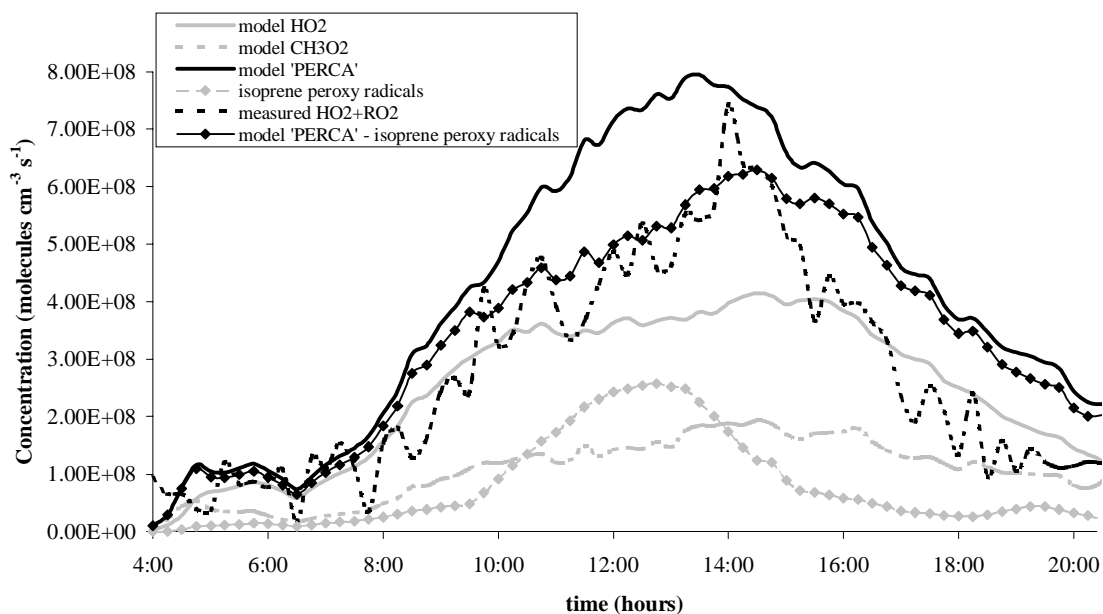


Figure 4 - Plot showing a breakdown of peroxy radicals on J199. The model 'PERCA' predictions are shown in black, with the actual measurements in dark grey. Note the asymmetry in the peroxy radical measurements around solar noon (see text). Model 'PERCA' – isoprene peroxy radicals (black dashed line), model HO₂ (dashed dark grey line), model CH₃O₂ (dashed light grey line), and isoprene peroxy radicals (solid light grey line). The peroxy radical measurements were made by Paul Monks, University of Leicester, UK.

Under clean conditions, the peroxy radical profile is symmetrical and tracks the solar flux. In order to understand the mechanistic origins of these effects, we have looked in some detail at the HO₂ production rate from various reaction channels in the isoprene scheme (Carslaw *et al.*, 1999c). Although the maximum production of HO₂ from some intermediate products in the isoprene scheme occurs around solar noon, Figure 5 shows that there are many intermediate products that are responsible for HO₂ production much later on. The position of these products in the isoprene oxidation scheme is shown in Figure 6. ISOPBO is an alkoxy radical produced when peroxy radicals, formed through the initial OH oxidation of isoprene, react with NO. Therefore, maximum HO₂ production occurs fairly close to the isoprene maximum. However, some of the intermediate products such as MVK, have a much longer lifetime than isoprene, and consequently, further breakdown products such as HMVKAO (oxy radical) are responsible for the later generation of peroxy radicals. Indeed, some of these HO₂ production routes continue to increase in magnitude throughout the afternoon (e.g. methylglyoxal, MGLYOX), reflecting their position in the degradation scheme. With many such routes producing HO₂, the observed asymmetry is easily understood.

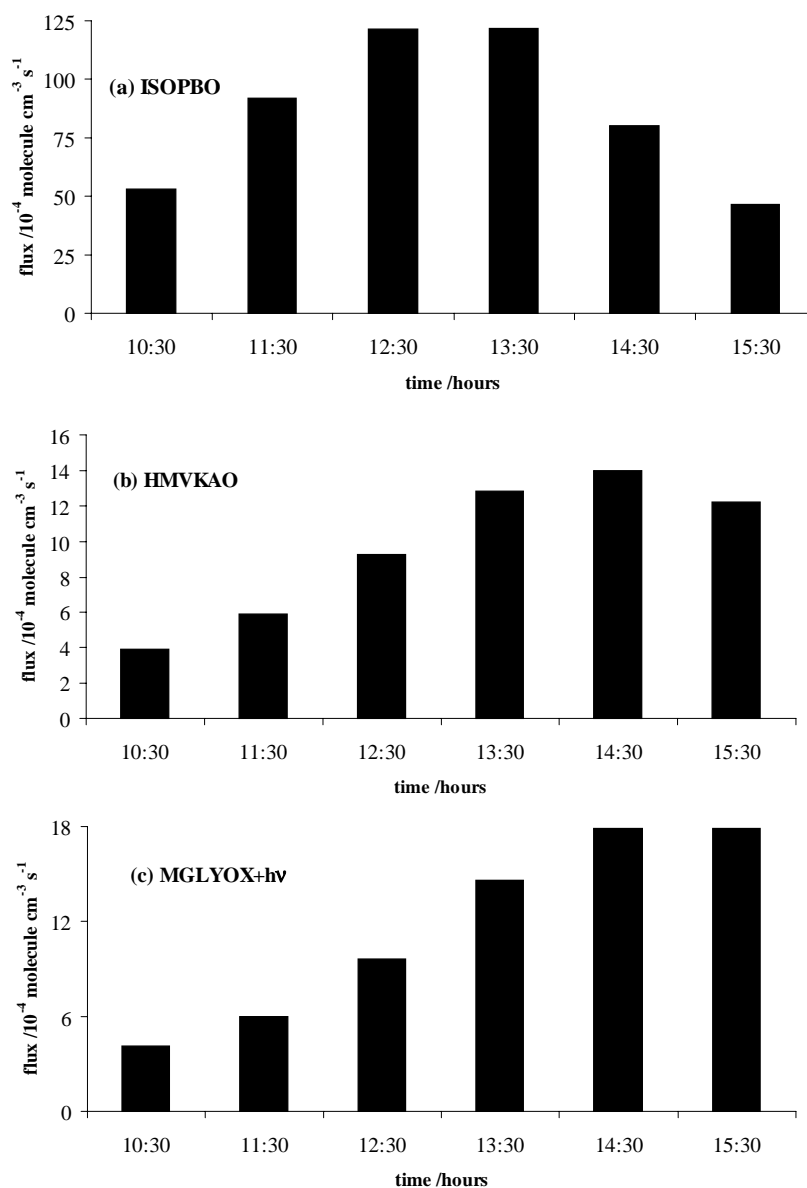


Figure 5 – Rate of formation of HO₂ from different oxidation steps in the isoprene mechanism.

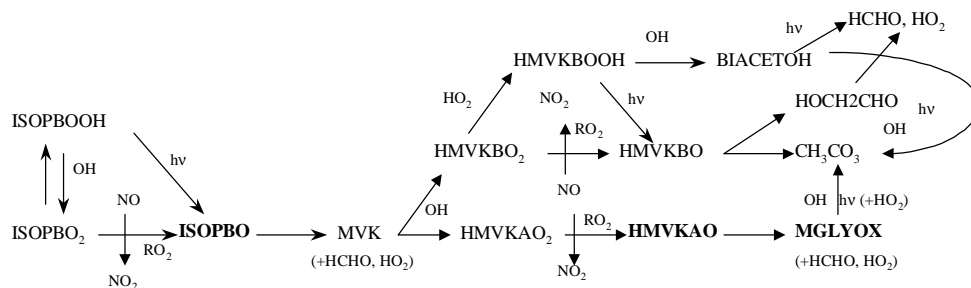


Figure 6 – Oxidation of isoprene through the MVK route (for a full explanation of all of the species, see Carslaw *et al.*, 1999c).

The role of formaldehyde in this context is particularly interesting. Figure 7 shows the formation of HO₂ from the isoprene degradation scheme throughout the day, and separately, the contribution from HCHO also formed through the isoprene scheme.

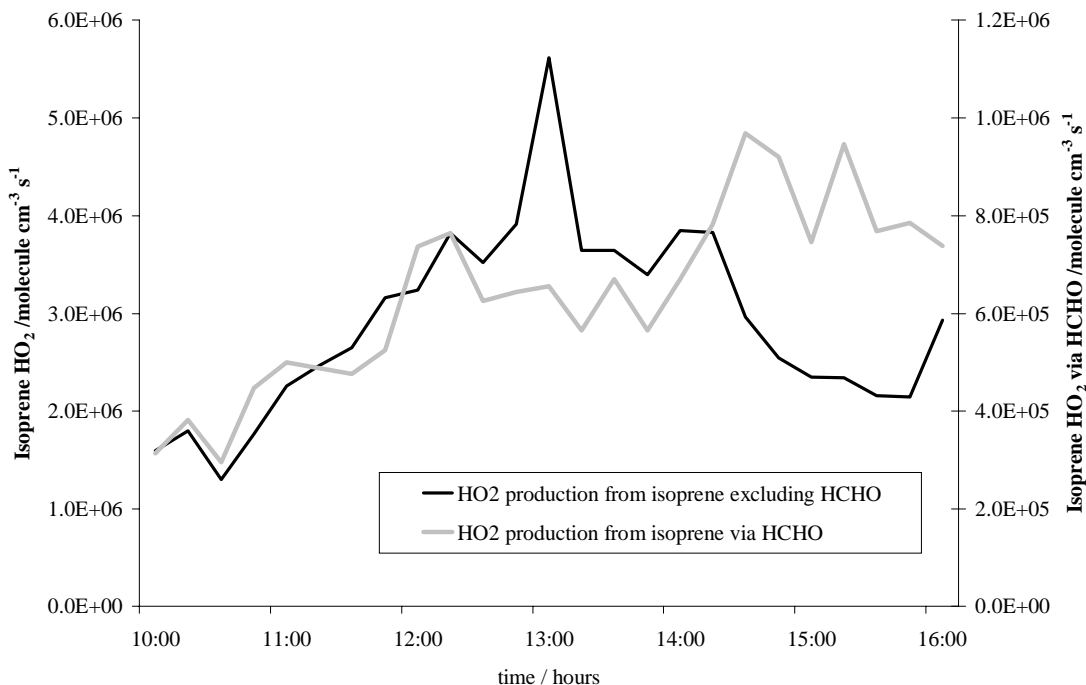


Figure 7 – HO₂ production from isoprene degradation, and shown separately, from isoprene-produced HCHO.

HCHO acts as a temporary reservoir for HO₂, locking it away until later in the afternoon. Interpretation of the data has also shown that isoprene is responsible for 40-60% of the HCHO formation, and 20-40% of the 2 ppb h⁻¹ conversion of NO to NO₂ (Carslaw *et al.*, 1999c). This analysis shows how accurate, time-resolved measurements of radical concentrations, coupled with a detailed mechanism, can be used to understand several aspects of the photochemical mechanism.

SOAPEX

Results from this campaign are at a preliminary stage. We show a model/measurement comparison of [OH] from February 7, 1999 in Figure 8, a typical baseline day.

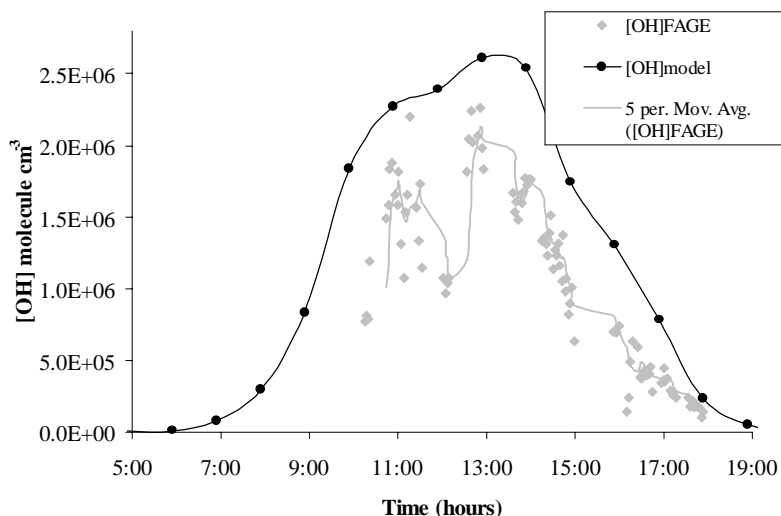


Figure 8 – Comparison of measured and modelled OH on 7th February, 1999. The FAGE measurements were made by Dwayne Heard, David Creasey and James Lee of the University of Leeds, UK.

SOAPEX was probably the most extensive campaign to date for the Leeds group in terms of number of observations, and we will be reporting further results in the near future.

Conclusions

The MCM has been used to model EUPHORE smog chamber data for systems including ethene, *n*-butane, toluene and α -pinene. The results are very encouraging and suggest that the MCM describes well smog chamber conditions. In addition, a methodology has been developed, based on the MCM, for constructing box models for simulating radical concentrations for comparison with field measurements. The model is constrained by field measurements of stable species and used to simulate OH, HO₂ and peroxy radicals. The comparisons with field measurements are reasonably satisfactory, although modelled [OH] is somewhat greater than measured [OH]. The detailed mechanism when coupled with atmospheric observations can be used to understand essential aspects of the atmospheric chemistry.

Acknowledgements

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