Development of the Master Chemical Mechanism (MCMv2.0) web site and recent applications of its use in tropospheric chemistry models

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Introduction

Atmospheric research in the School of Chemistry (Leeds) involves several groups working in closely related areas, studying a wide variety of topics of relevance to atmospheric processes. The Tropospheric Chemistry Modelling group is involved with all aspects of model construction and application. Part of this work has been a collaborative project, funded by the UK Department of the Environment, Transport and the Regions (DETR), to develop and apply predictive models to the formation of tropospheric ozone on a range of different geographical scales (i.e. global, regional and national). The insight gained in this manner can aid in the formulation of policy with regards to the air quality and ambient levels of ozone in the United Kingdom. The master chemical mechanism (MCM) underpins much of the current ozone modelling undertaken on the behalf of the DETR.

The main intention of the web site is to provide a flexible, easily utilised platform for the MCM that is readily accessed by the whole research community, and to promote its collaborative development and evaluation. This paper details updates and developments that have occurred since the launch of the MCMv1.0 web site (Saunders *et al.* 1997). The current MCMv2.0 consists of around 10500 reactions and 3500 species and the web site is located at:

http://chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html

MCM chemistry updates

The degradation schemes of MCMv1.0 have been revised and updated in several areas. The inorganic chemistry section and generalized rate parameters have been completely reviewed. Updates incorporate data available in the open literature through 1997, including the evaluations in the IUPAC (Atkinson *et al.*, 1997a, 1997b) and JPL (DeMore *et al.*, 1997) publications.

Photolysis parameter updates have been made using a newly developed UV-flux model (*photol*) with an improved representation of the effect of elevated concentrations of particles, ozone and nitrogen dioxide in the boundary layer. An important revision has been the incorporation of recently published quantum yields for ozone photolysis. Details of the model calculations are given in an earlier project report (Jenkin *et al.*, 1997). Revised parameters are now available, which define the photolysis rate as a function of solar zenith angle for 28 reactions, for conditions appropriate to the boundary layer over NW Europe.

The schemes for aromatic VOC have been completely revised since MCMv1.0, to take account of data available in the open literature through July 1997 (eg. Yu and Jeffries, 1997; Carter *et al.*, 1995; Wiesen *et al.*, 1995; Klotz *et al.*, 1995, 1997). Full details of the supplementary protocol implemented for the aromatic mechanism construction are presented in Jenkin *et al.* (1997) and are summarised on the web site.

Recently reported kinetic and mechanistic information relevant to the degradation of organic oxygenates has been used to update the MCMv1.0 schemes for alcohols, glycols, ethers, glycol ethers ands esters. Details of the construction are given in Jenkin *et al.* (1997) and in the open literature (Jenkin and Hayman, 1999)

New VOC schemes in MCMv2.0

The primary VOC list of MCMv1.0 has been extended to include two of the proposed fuel additives, dimethoxy methane and dimethyl carbonate. In addition, a degradation scheme has been constructed for α-pinene, in order to give a representation of a monoterpene. The complete VOC list now totals 123 VOC species, segregated into the classifications given in Table 1. In addition, there is a comprehensive inorganic scheme.

Table 1 - Classification of the 123 primary VOC of MCMv2.0

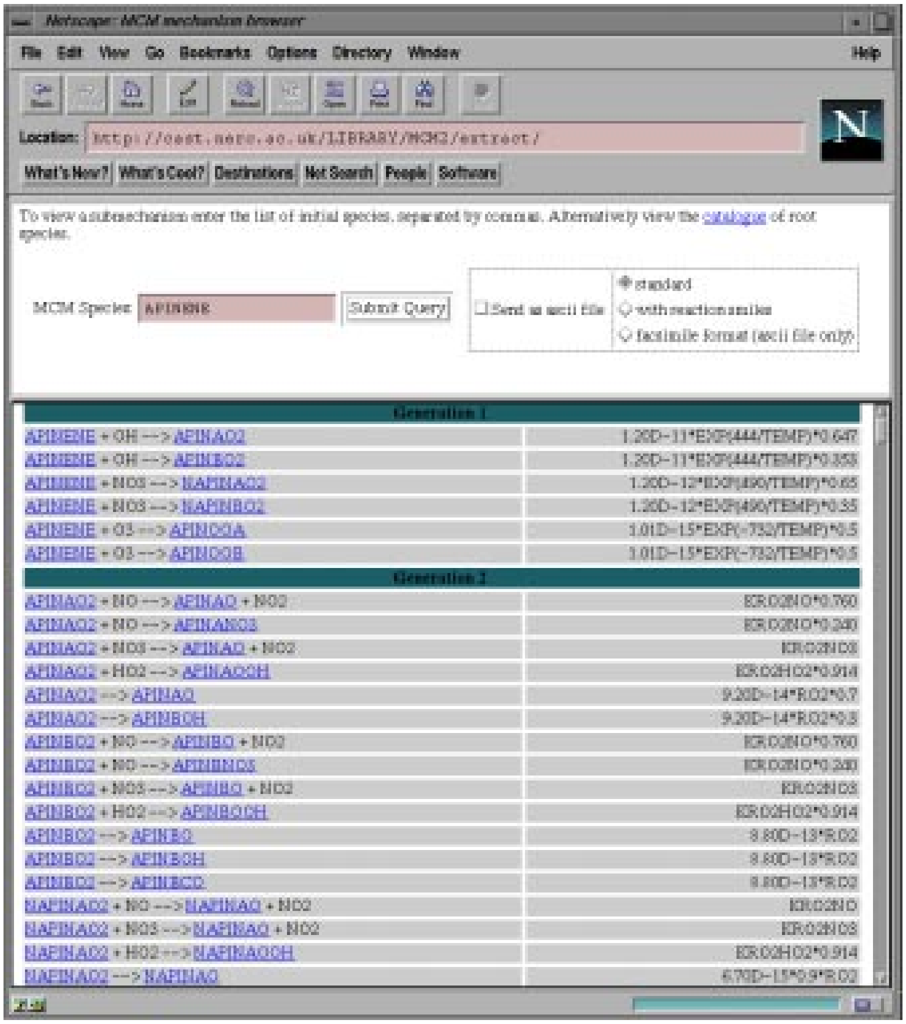
Classification	Number of species
Alkanes	22
Alkenes	15
Dialkenes	2
Alkynes	1
Aromatics	18
Aldehydes	6
Ketones	10
Alcohols and Glycols	17
Ethers and Glycol ethers	10
Esters	8
Organic acids	3
Other Oxygenates	2
Monoterpenes	1
Chloro-carbons	8

MCMv2.0 web site

On entering the web site, the home page shows a menu of contents and some general introduction. Details of the MCM project, degradation scheme construction protocol and recent developments are located within the project description area, under the following section headings:

- *Project Description*
- *Project Objectives*
- *Introduction to the Master Chemical Mechanism (MCM)*
- *Development of the MCMv2.0*
- *Construction of the MCMv2.0*
- *Brief Protocol Review*
- *Aromatic scheme development*

The *What's New* button shows the user which changes and additions have been made to the original MCMv1.0 site. New features of the system are highlighted, including the MCM subset assembler tool, a facility to enable the assembly of subsets of MCMv2.0. The MCM subset assembler tool allows the user to select any number of compounds from the primary VOC list, and extract a complete, consistent, degradation mechanism for that subset (Figure 1).



To view a submechanism enter the list of initial species, separated by commas. Alternatively view the catalogue of root species.

MCM Species: APINENE [Submit Query]

☐ Send as ascii file

● standard
○ with reaction smiles
○ facsimile format (ascii file only)

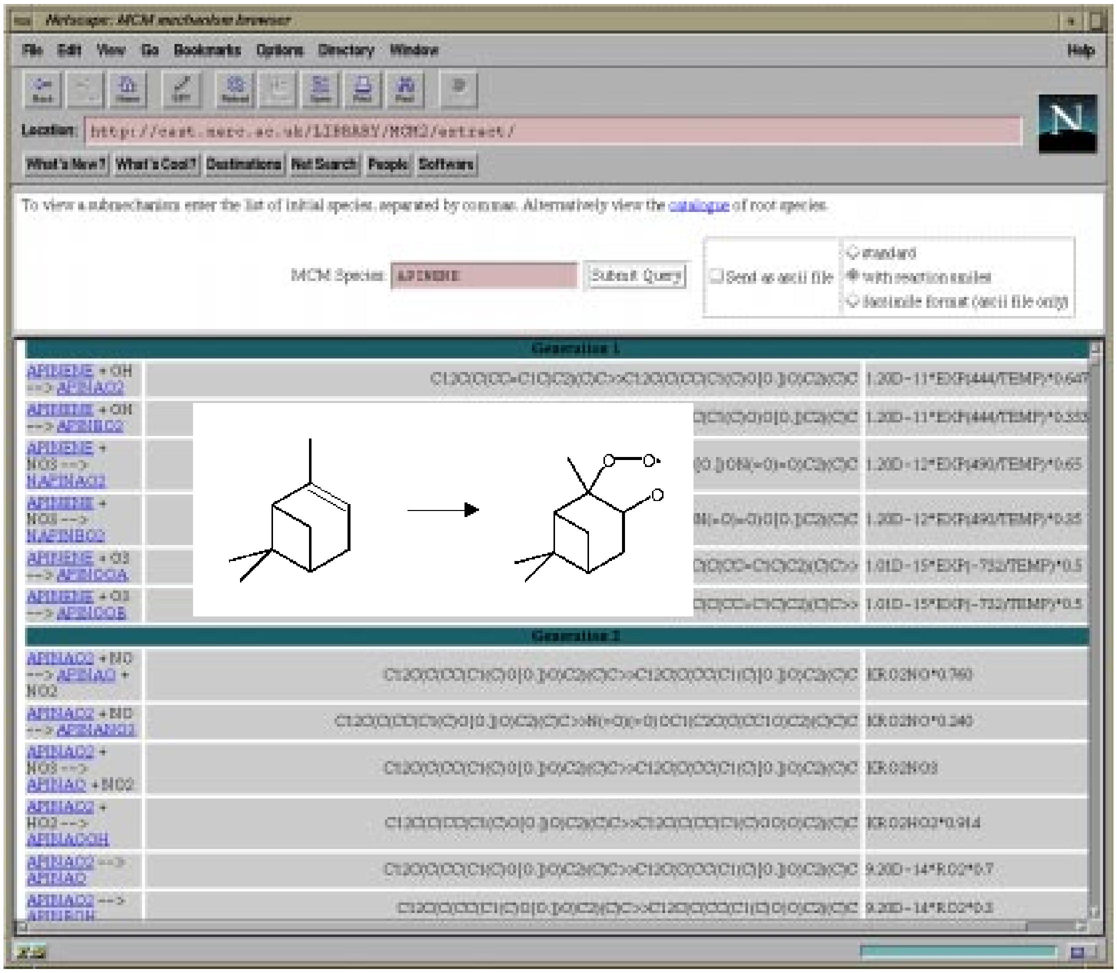
Generation 1	
APINENE + OH --> APINAO2	1.20D-11*EXP(444/TEMP)*0.647
APINENE + OH --> APINBO2	1.20D-11*EXP(444/TEMP)*0.353
APINENE + NO3 --> NAPINAO2	1.20D-12*EXP(490/TEMP)*0.65
APINENE + NO3 --> NAPINBO2	1.20D-12*EXP(490/TEMP)*0.35
APINENE + O3 --> APINOOA	1.01D-15*EXP(-732/TEMP)*0.5
APINENE + O3 --> APINOOB	1.01D-15*EXP(-732/TEMP)*0.5
Generation 2	
APINAO2 + NO --> APINAO + NO2	KRO2NO*0.760
APINAO2 + NO --> APINANO3	KRO2NO*0.240
APINAO2 + NO3 --> APINAO + NO2	KRO2NO3
APINAO2 + HO2 --> APINAOOH	KRO2HO2*0.914
APINAO2 --> APINAO	9.20D-14*RO2*0.7
APINAO2 --> APINBOH	9.20D-14*RO2*0.3
APINBO2 + NO --> APINBO + NO2	KRO2NO*0.760
APINBO2 + NO --> APINBNO3	KRO2NO*0.240
APINBO2 + NO3 --> APINBO + NO2	KRO2NO3
APINBO2 + HO2 --> APINBOOH	KRO2HO2*0.914
APINBO2 --> APINBO	8.80D-13*RO2
APINBO2 --> APINBOH	8.80D-13*RO2
APINBO2 --> APINBCO	8.80D-13*RO2
NAPINAO2 + NO --> NAPINAO + NO2	KRO2NO
NAPINAO2 + NO3 --> NAPINAO + NO2	KRO2NO3
NAPINAO2 + HO2 --> NAPINAOOH	KRO2HO2*0.914
NAPINAO2 --> NAPINAO	6.70D-15*0.9*RO2

Figure 1 - The subset assembler tool extracting the degradation scheme for α-pinene.

Changes have also been made to the MCM archive. The archive download area now includes a repository of the files available on the MCMv1.0 web site, and a new file store of facsimile codes, which incorporate the current MCMv2.0 data set.

MCM web site developments

Work is continuing to further improve the web site. One improvement will be the enhancement of the subset assembler tool. In addition, there will be improved species and reaction visualisation for multi-platform use throughout the site. For instance, Figure 2 shows a visual display of the reaction within the subset assembler tool. This new development will not require the set up of a helper application for the internet browser in use.



Location: http://cast.nerc.ac.uk/LIBRARY/MCM2/extract/

To view a submechanism enter the list of initial species, separated by commas. Alternatively view the catalogue of root species.

MCM Species: APINENE Submit Query

☐ Send as ascii file

○ standard
● with reaction smiles
○ facsimile format (ascii file only)

APINENE + OH --> APINAO2	1.20D-11*EXP(444/TEMP)*0.647
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APINAO2 + NO --> APINAO + NO2	KRO2NO*0.760
APINAO2 + NO --> APINANO3	KRO2NO*0.240
APINAO2 + NO3 --> APINAO + NO2	KRO2NO3
APINAO2 + HO2 --> APINAOOH	KRO2HO2*0.914
APINAO2 --> APINAO	9.20D-14*RO2*0.7
APINAO2 -->	9.20D-14*RO2*0.3

Figure 2. Platform independent display of reaction structures

We also hope to make MCMv2.0 and the accompanying models on the web site, available in Fortran code in the near future.

MCM maintenance and development

The degradation schemes for aromatic hydrocarbons will be updated in line with new kinetic and mechanistic data, as they become available. The particular features of aromatic degradation which have the most influence on ozone formation will be identified by performing appropriate POCP sensitivity studies.

The representation of a number of gas-phase chemical processes will be updated in line with recently published kinetic and mechanistic data. In particular, the following reactions:

- the reactions of OH with PAN species

- the reactions of oxy radicals formed from the degradation of esters and alkenes
- the formation of excited oxy radicals from the reactions of some peroxy radicals with NO.

In addition, we will also be updating the photolysis rates of ozone and other inorganic and organic species in line with the latest absorption cross-section and quantum yield data. We will also investigate the feasibility of incorporating or improving the description of the formation of secondary sulphate and nitrate aerosols, in order to improve the representation of important heterogeneous processes (e.g. the reaction of N_2O_5 with water).

MCM recent applications

The MCM code is being used in a wide range of tropospheric models. Recent applications include the following work:

- An investigation of the sensitivity of POCPs for oxygenated organic compounds to variations in kinetic and mechanistic parameters (Jenkin and Hayman, 1999)
- POCPs for 123 organic compounds under north American conditions calculated with the MCMv2.0. (Derwent *et al.*, 1999a)
- Comparison of modelled OH, HO_2 and RO_2 concentrations using the MCM with measurements in the marine boundary layer (Carslaw *et al.*, 1999a,b)
- Detailed study of isoprene chemistry using the MCM (Carslaw *et al.*, 1999c)
- Hydroxyl radical concentrations estimated from measurements of trichloroethylene during the EASE/ACSOE campaign at Mace Head, Ireland during July 1996. (Derwent *et al.* 1999b)

References

Atkinson R., D.L. Baulch, R.A. Cox, R.F. Hampson, J.A.Kerr, M.J. Rossi and J. Troe (1997a) Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement V. *J. Phys. Chem. Ref. Data*, **26**, p521-1011.

Atkinson R., D.L. Baulch, R.A. Cox, R.F. Hampson, J.A.Kerr, M.J. Rossi and J. Troe (1997b) Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement VI. *J. Phys. Chem. Ref. Data*, **26**, 1329-1499.

Carter W.P.L., D. Luo, I.L. Malkina and J.A. Pierce (1995) Project ME-9, Environmental chamber studies of atmospheric reactivities of VOC. *California air resources board* contract A032-0692, and *south coast air quality management* contract C91323.

Carslaw N., D.J. Creasey, D.E. Heard, A.C. Lewis, J.B. McQuaid, M.J. Pilling, P.S. Monks, B.J. Bandy and S.A. Penkett (1999a) Modelling OH, HO_2 and RO_2 radicals in the marine boundary layer: 1. Model construction and comparison with measurements. *J. Geophys. Res.* **-** in press.

Carslaw N., P.J. Jacobs and M.J. Pilling (1999b), Modelling OH, HO_2 and RO_2 radicals in the marine boundary layer: 2. Mechanism reduction and uncertainty analysis, submitted to *J. Geophys. Res.* in press.

Carslaw N., N. Bell, A.C. Lewis, J.B. McQuaid and M.J. Pilling (1999c), A detailed study of isoprene chemistry during the EASE96 Mace Head campaign: July 17th 1996, a case study, submitted to *Atmospheric Environment*.

Derwent R.G., M.E. Jenkin, S.M. Saunders and M.J. Pilling (1999a) Photochemical ozone creation potentials for 123 organic compounds under north American conditions calculated with the Master Chemical Mechanism v2.0 **-** *California Air Resources Board.*

Derwent R.G., N. Carslaw, P.G. Simmonds, M. Bassford, S. O'Doherty, D. Ryall, M.J. Pilling, A.C. Lewis and J.B. McQuaid (1999b) Hydroxyl radical concentrations estimated from measurements of trichloroethylene during the EASE/ACSOE campaign at Mace Head, Ireland during July 1996. *J. Atmos. Chem.*, **34**, p185.

Jenkin M.E., G.D. Hayman (1999) Photochemical Ozone creation potentials for oxygenated organic compounds: sensitivity to variations in kinetic and mechanistic parameters. *Atmospheric Environment*, **33**, 1275-1293.

Jenkin M.E., G.D. Hayman, R.G. Derwent, S.M. Saunders and M.J. Pilling (1997) Tropospheric chemistry modelling: Improvements to current models and application to policy issues. 1st annual report AEA/RAMP/20150/R001.

Klotz B.G., A. Bierbach, I. Barnes and K.H. Becker (1995) Kinetic and mechanistic study of the atmospheric chemistry of muconaldehydes. *Environ. Sci. and Technol.*, **29**, p2322.

Klotz B.G., A. Bierbach, I. Barnes, K.H. Becker and B.T. Golding (1997) Atmospheric chemistry of benzene oxide/oxepin. *Chem. Soc. Faraday Trans*., **93**, p1507.

Saunders S.M., M.E. Jenkin, R.G. Derwent and M.J. Pilling (1997) Report Summary: World Wide Web site of a Master Chemical Mechanism (MCM) for use in tropospheric chemistry models. *Atmospheric Environment*, **31**, p1249.

Wiesen E., I. Barnes and K.H. Becker (1995) Study of the OH-initiated degradation of the aromatic photooxidation product 3,4-dihydroxy-3-hexene-2,5-dione. *Environ. Sci. and Technol*., **29**, p1830.

Yu J. and H.E. Jeffries (1997) Atmospheric photoxidation of alkylbenzenes. *Atmospheric Environment*, **31**, 2281-2287.