

A Comparison of Chemical Mechanisms using Tagged Ozone Production Potential (TOPP) Analysis: Supplementary Material

J. Coates¹ and T. Butler¹

¹Institute for Advanced Sustainability Studies, Potsdam, Germany

December 3, 2014

S1 Introduction

This is the supplementary material to the research paper “A Comparison of Chemical Mechanisms using Tagged Ozone Production Potential (TOPP) Analysis” and provides further information about the methodology as well as additional analysis.

S2 Mechanism Setup

All chemical mechanisms were adapted from their original format into the modularised KPP (Damian et al., 2002) format for use in the MECCA boxmodel (Sander et al., 2005) as modified by (Butler et al., 2011).

The MCM v3.2 (Jenkin et al., 1997, 2003; Saunders et al., 2003; Bloss et al., 2005; Rickard et al., 2014) is the reference mechanism and its approach to dry deposition, photolysis and peroxy radical–peroxy radical reactions were applied to all mechanisms.

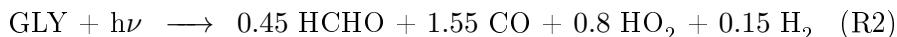
S2.1 Photolysis

Photolysis was parameterised as a function of the solar zenith angle following the MCM approach (Saunders et al., 2003). Species from reduced mechanisms with a direct

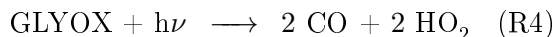
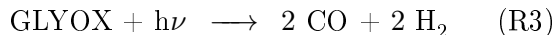
counterpart in the MCM v3.2 were assigned the corresponding MCM v3.2 photolysis rate
 22 parameter. Otherwise, the recommended rate parameter in the mechanism determined the
 appropriate MCM v3.2 photolysis rate parameter. In some cases, the MCM v3.2 photolysis
 24 rate parameter closest in magnitude to that specified by the mechanism.

For example, the organic nitrate species ONIT in RACM2 has a photolysis rate
 26 parameter of $1.96 \times 10^{-6} \text{ s}^{-1}$ that was compared to the MCM v3.2 organic nitrate photolysis
 rate parameters ($J_{51} - J_{57}$). The rate parameter J_{54} is the most similar in magnitude and
 28 was assigned as the ONIT photolysis rate parameter in RACM2.

Photolysis reactions of a species in reduced mechanisms were sometimes represented
 30 by more than one MCM v3.2 photolysis reaction. The product yields of the original
 mechanism reactions were preserved using combinations of the MCM v3.2 rate parameters.
 32 This approach was used for glyoxal photolysis in RADM2, which is described by (R1) and
 (R2).



Whereas in the MCM v3.2, (R3), (R4) and (R5) are prescribed for glyoxal photolysis with
 36 the rates J_{31} , J_{32} and J_{33} respectively.



38 The product yields in (R1) were retained using a photolysis rate parameter of
 $0.87 J_{31} + 0.13 J_{32}$, whilst for (R2) the rate $0.15 J_{31} + 0.45 J_{32} + 0.4 J_{33}$ was used. Table
 40 S1 illustrates the product yield calculations.

S2.2 Organic Peroxy Radical Self and Cross Reactions

42 Reactions of organic peroxy radicals (RO_2) with other organic peroxy radicals are
 divided into self ($\text{RO}_2 + \text{RO}_2$) and cross ($\text{RO}_2 + \text{R}'\text{O}_2$) reactions. These reactions are
 44 typically represented in chemical mechanisms as bimolecular reactions which would cause
 ambiguities when implementing the tagging scheme. Namely, which tag to be used for
 46 the products of reactions between RO_2 reactants having different tags. The MCM v3.2

	Rate Parameter	MCM v3.2 Products and Yields
(R1)	0.87 J ₃₁	1.74 CO + 0.87 H ₂
	0.13 J ₃₂	0.13 CO + 0.13 HCHO
	0.87 J ₃₁ + 0.13 J ₃₂	1.87 CO + 0.13 HCHO + 0.87 H ₂
(R2)	0.15 J ₃₁	0.30 CO + 0.15 H ₂
	0.45 J ₃₂	0.45 CO + 0.45 HCHO
	0.4 J ₃₃	0.80 CO + 0.80 HO ₂
	0.15 J ₃₁ + 0.45 J ₃₂ + 0.4 J ₃₃	1.55 CO + 0.45 HCHO + 0.80 HO ₂ + 0.15 H ₂

Table S1: Calculation of glyoxal MCM v3.2 photolysis rate parameters retaining RADM2 glyoxyl photolysis product yields.

Mechanism	Reaction	Rate Constant
MCM v3.2	C2H5O2 = C2H5O	$k^*RO_2*0.6 \text{ s}^{-1}$
	C2H5O2 = C2H5OH	$k^*RO_2*0.2 \text{ s}^{-1}$
	C2H5O2 = CH3CHO	$k^*RO_2*0.2 \text{ s}^{-1}$
MOZART-4	C2H5O2 + CH3O2 = 0.7 CH2O + 0.8 CH3CHO + HO2 + 0.3 CH3OH + 0.2 C2H5OH	$2 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
	C2H5O2 + C2H5O2 = 1.6 CH3CHO + 1.2 HO2 + 0.4 C2H5OH	$6.8 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
MOZART-4 modified	C2H5O2 = 0.8 CH3CHO + 0.6 HO2 + 0.2 C2H5OH	$2 \times 10^{-13}*RO_2 \text{ s}^{-1}$

Table S2: Ethyl peroxy radical (C₂H₅O₂) self and cross organic peroxy reactions in MCM v3.2 and MOZART-4 including rate constants. $k = 2(6.6 \times 10^{-27} \exp(365/T))^{\frac{1}{2}} \text{ molecules}^{-1} \text{ s}^{-1}$ and RO₂ is the sum of all organic peroxy radical mixing ratios.

Reactants	Products	Rate Constant
MO2 + MO2	0.74 HO2 + 1.37 HCHO + 0.63 MOH	$9.4 \times 10^{-14} \exp(390/T) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
MO2	0.37 HO2 + 0.685 HCHO + 0.315 MOH	$9.4 \times 10^{-14} \exp(390/T)*RO_2 \text{ s}^{-1}$
ETHP + MO2	HO2 + 0.75 HCHO + 0.75 ACD + 0.25 MOH + 0.25 EOH	$1.18 \times 10^{-13} \exp(158/T) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
ETHP	0.63 HO2 + 0.065 HCHO + 0.75 ACD + 0.25 EOH	$1.18 \times 10^{-13} \exp(158/T)*RO_2 \text{ s}^{-1}$

Table S3: Dermination of ETHP pseudo-unimolecular reaction and rate constant in RACM2 including rate constants. RO₂ is the sum of all organic peroxy radical mixing ratios.

approach to self and cross RO_2 reactions (each RO_2 species reacts with the pool of all other RO_2 at a single uniform rate) is used to avoid such ambiguities. The MCM v3.2 approach represents RO_2 - RO_2 reactions as a pseudo-unimolecular reaction whose rate constant includes a factor 'RO2' which is the sum of the mixing ratios of all organic peroxy radicals (Saunders et al., 2003).

The pseudo-unimolecular reaction products and their yields were determined by one of two methods. Firstly, by using the $\text{RO}_2 + \text{RO}_2$ reaction and halving the product yields, demonstrated for the MOZART-4 treatment of the ethyl peroxy radical in Table S2. Alternatively, the $\text{RO}_2 + \text{CH}_3\text{O}_2$ reaction was used to determine the products due to CH_3O_2 and these products are then removed.

Table S3 demonstrates the steps determining the ETHP pseudo-unimolecular reaction in RACM2. First the products due to MO_2 (CH_3O_2 in RACM2) are determined as outlined previously using the $\text{MO}_2 + \text{MO}_2$ reaction. The MO_2 product yields are subtracted from the $\text{ETHP} + \text{MO}_2$ reaction. Any products having a negative yield are not included in the final pseudo-unimolecular reaction.

The methyl acyl peroxy radical ($\text{CH}_3\text{C}(\text{O})\text{O}_2$) was the exception to the above approach. Although most mechanisms include a $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2$ reaction, the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ pseudo-unimolecular reaction was derived by subtracting the CH_3O_2 product yields from the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{O}_2$ reaction. This approach was used as the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{O}_2$ reaction is the most significant reaction for $\text{CH}_3\text{C}(\text{O})\text{O}_2$.

The rate constant for each pseudo-unimolecular reaction was taken as that of the $\text{RO}_2 + \text{CH}_3\text{O}_2$ reaction multiplied by an 'RO2' factor, which is the sum of the mixing ratios of all organic peroxy radicals. The $\text{RO}_2 + \text{CH}_3\text{O}_2$ rate constant was chosen as this is the most likely reaction to occur.

Model runs using the original and modified approach to the RO_2 - RO_2 reactions for each mechanism were performed. The resulting O_3 concentration time series were compared and are shown in Figure S1.

S2.3 Dry Deposition

Dry deposition velocities are taken from the MCM v3.2. The MCM v3.2 dry deposition velocities of the same chemical functional group were used for mechanism species without

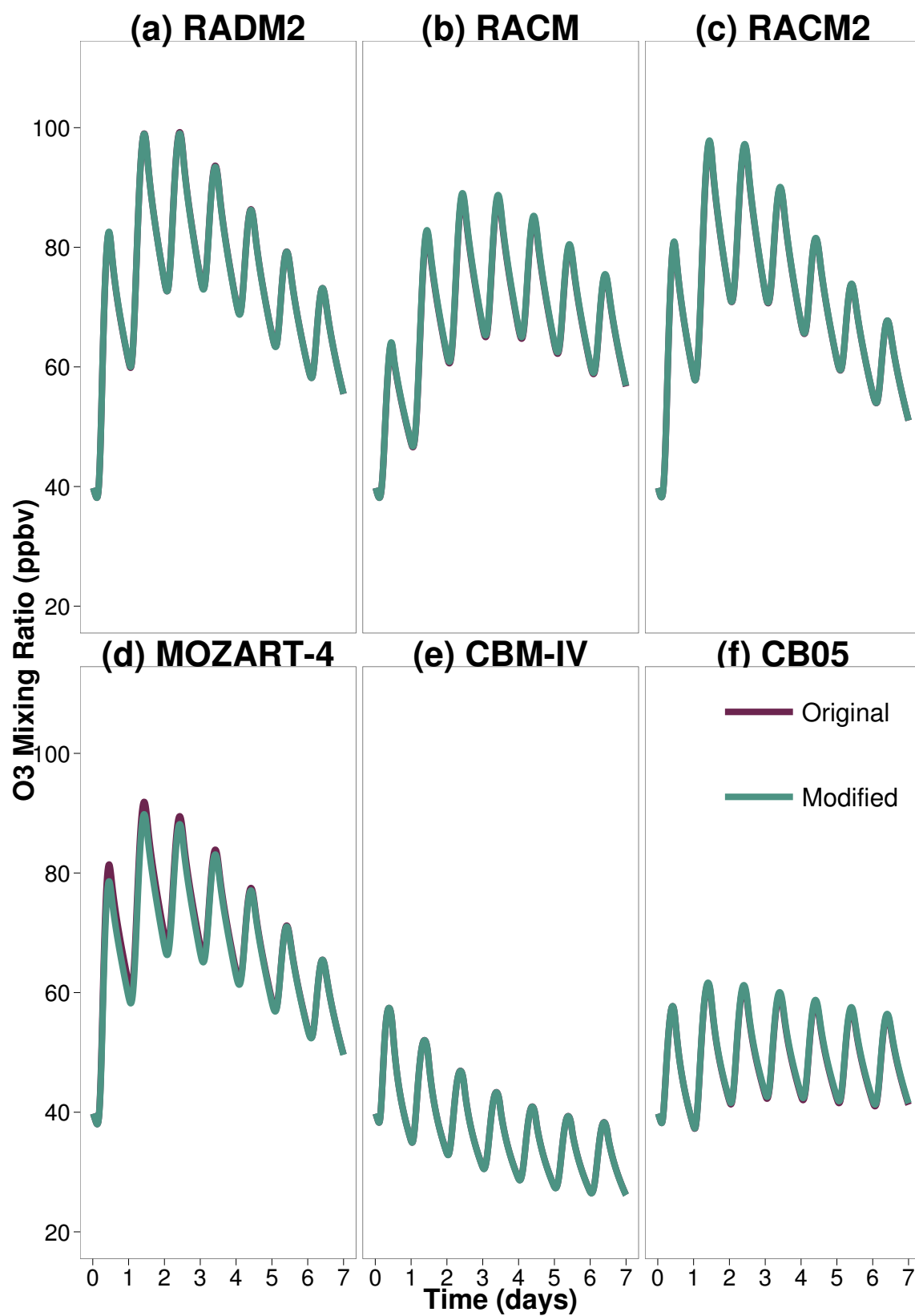


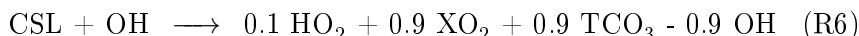
Figure S1: The time series of the O₃ for the reduced mechanisms using the original and modified approach to RO₂-RO₂ reactions

direct MCM v3.2 analogues. For example, the dry deposition velocity of PAN-like species
 78 in all mechanisms was equivalent to that of the PAN species in the MCM v3.2.

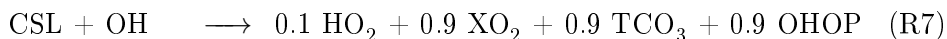
S2.4 Negative Product Yield Treatment

80 Some mechanisms include reactions where products have a negative yield. These reactions
 were re-written including an operator species with a positive yield, as the analysis tools
 82 used in this study do not allow negative product yields. The operator species acts as a
 sink for the original product by immediately reacting with the original product generating
 84 a ‘NULL’ product.

For example, in RADM2 the OH + CSL (cresol) reaction has negative OH yield in
 86 (R6) (Stockwell et al., 1990).



88 The negative OH yield was adapted to a positive operator (OHOP) yield in (R7). OHOP
 then reacts immediately with OH giving a ‘NULL’ product with a rate constant of
 90 $8.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (R8). Thus preserving the OH yields from (R6) in RADM2.



92 S3 Mapping Emitted NMVOC to Mechanism Species

The emitted NMVOC are typical of Los Angeles as described in Baker et al. (2008). The
 94 MCM v3.2, v3.1 (Jenkin et al., 1997; Saunders et al., 2003; Jenkin et al., 2003) and CRI v2
 (Jenkin et al., 2008) explicitly represent all of these NMVOC.

96 NMVOC representation in all other mechanisms required mapping to specific
 mechanism species. This mapping followed the recommendations on the literature of
 98 the mechanism. Table S4 describes the mechanism species used for mapping the initial
 NMVOC. Table 2 of the main article shows the final mapping of each NMVOC to each
 100 mechanism species.

S4 Extra Plots

Mechanism	Species	Description	Mechanism	Species	Description
MOZART-4 (Emmons et al., 2010)	C2H6	Ethane	RACM2 (Goliff et al., 2013)	ETH	Ethane
	C3H8	Propane		HC3	OH rate constant (298 K, 1 atm) less than 3.4×10^{-12} $\text{cm}^3 \text{s}^{-1}$
	BIGALK	Lumped alkanes C > 3		HC5	OH rate constant (298 K, 1 atm) between 3.4×10^{-12} and 6.8×10^{-12} $\text{cm}^3 \text{s}^{-1}$
	C2H4	Ethene		HC8	OH rate constant (298 K, 1 atm) greater than 6.8×10^{-12} $\text{cm}^3 \text{s}^{-1}$
	C3H6	Propene		ETE	Ethene
	BIGENE	Lumped alkenes C > 3		OLT	Terminal alkenes
	ISOP	Isoprene		OLI	Internal alkenes
	TOLUENE	Lumped aromatics		ISO	Isoprene
	ETH	Ethane		BEN	Benzene
	HC3	OH rate constant (298, 1 atm) between 2.7×10^{-13} and 3.4×10^{-12}		TOL	Toluene and less reactive aromatics
RADM2 (Stockwell et al., 1990)	HC5	OH rate constant (298, 1 atm) between 3.4×10^{-12} and 6.8×10^{-12}	CBM-IV (Gery et al., 1989)	XYM	m-Xylene
	HC8	OH rate constant (298, 1 atm) greater than 6.8×10^{-12}		XYO	o-Xylene
	OL2	Ethene		XYP	p-Xylene
	OLT	Terminal Alkenes		PAR	Paraffin carbon bond C-C
	OLI	Internal Alkenes		ETH	Ethene
	ISO	Isoprene		OLE	Olefinic carbon bond C=C
	TOL	Toluene and less reactive aromatics		ALD2	High molecular weight aldehydes
	XYL	Xylene and more reactive aromatics		ISOP	Isoprene
	ETH	Ethane		TOL	Toluene
	HC3	OH rate constant (298 K, 1 atm) less than 3.4×10^{-12} $\text{cm}^3 \text{s}^{-1}$		XYL	Xylene
RACM (Stockwell et al., 1997)	HC5	OH rate constant (298 K, 1 atm) between 3.4×10^{-12} and 6.8×10^{-12} $\text{cm}^3 \text{s}^{-1}$	CB05 (Yarwood et al., 2005)	FORM	Formaldehyde
	HC8	OH rate constant (298 K, 1 atm) greater than 6.8×10^{-12}		ETHA	Ethane
	ETE	Ethene		PAR	Paraffin carbon bond C-C
	OLT	Terminal alkenes		OLE	Terminal olefin carbon bond R-C=C
	OLI	Internal alkenes		FORM	Formaldehyde
	ISO	Isoprene		ISOP	Isoprene
	TOL	Toluene and less reactive aromatics		TOL	Toluene and other monoalkyl aromatics
	XYL	Xylene and more reactive aromatics		XYL	Xylene and other polyalkyl aromatics
	ETH	Ethane			
	HC3	OH rate constant (298 K, 1 atm) less than 3.4×10^{-12} $\text{cm}^3 \text{s}^{-1}$			

Table S4: Description of primary mechanism species used for mapping emitted NMVOCs.

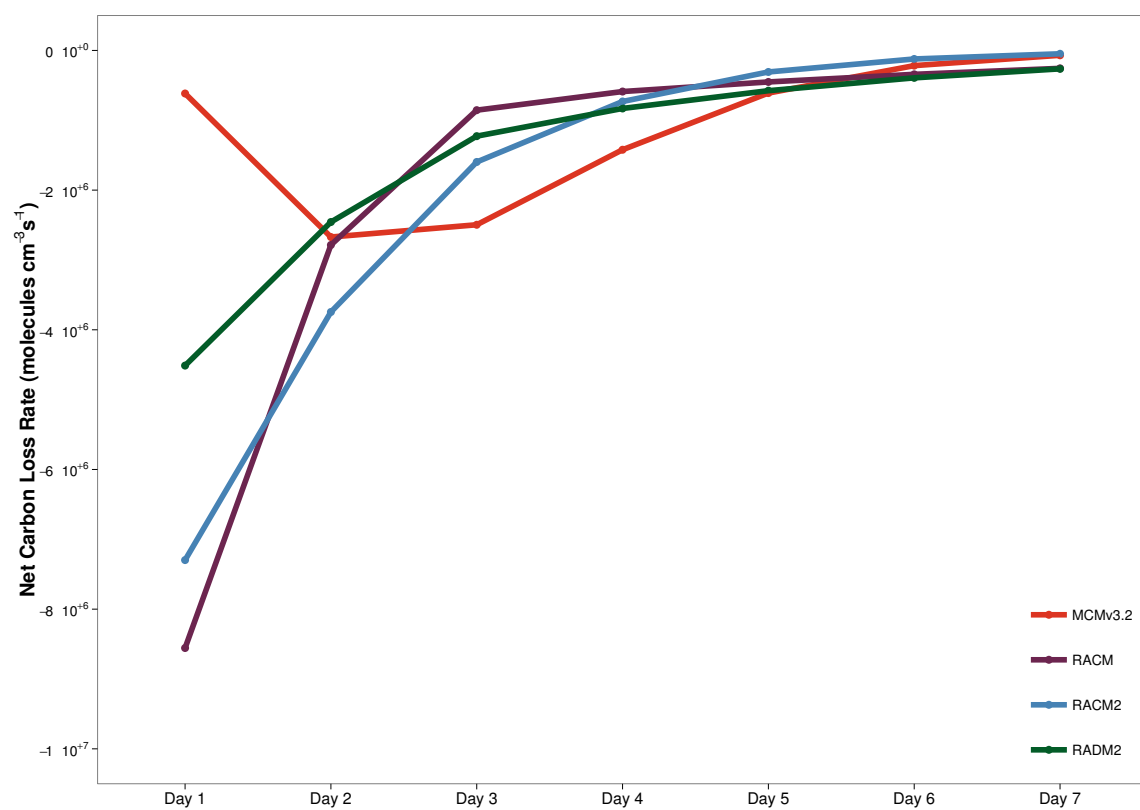


Figure S2: Day-time reactive carbon loss during octane degradation in RADM2, RACM and RACM compared to MCM v3.2.

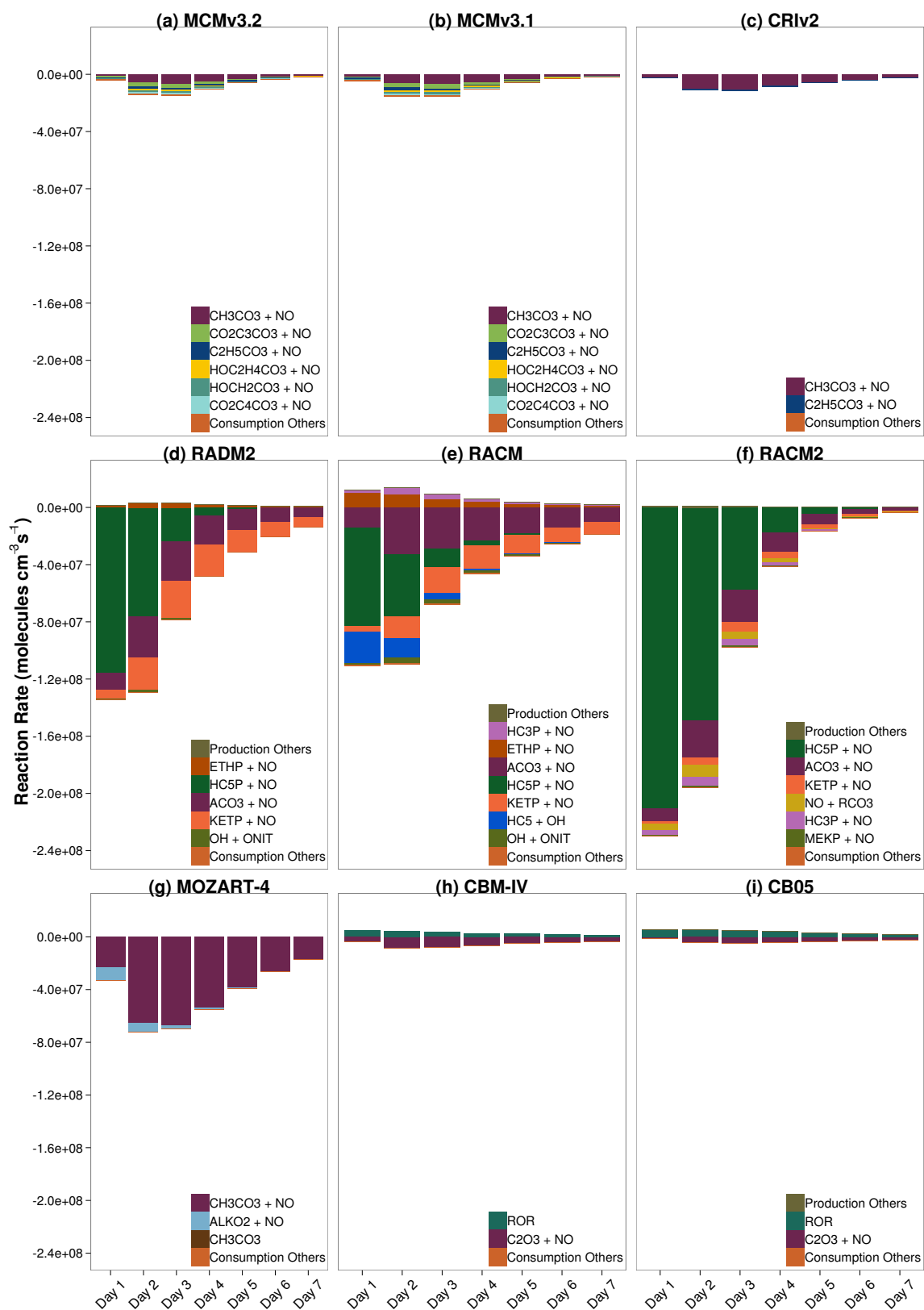


Figure S3: Reactions responsible for day-time reactive carbon loss during pentane degradation.

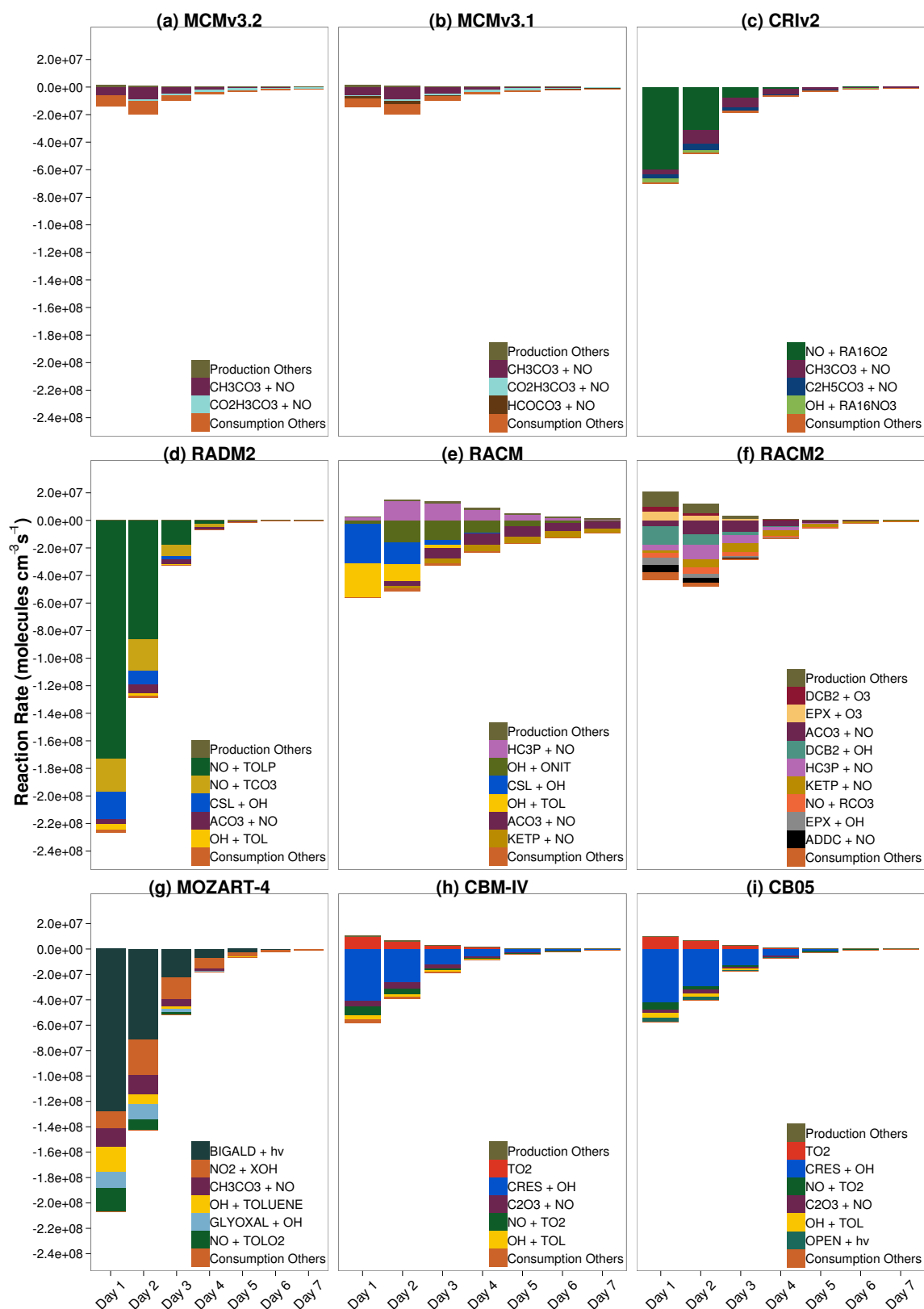


Figure S4: Reactions responsible for day-time reactive carbon loss during toluene degradation.

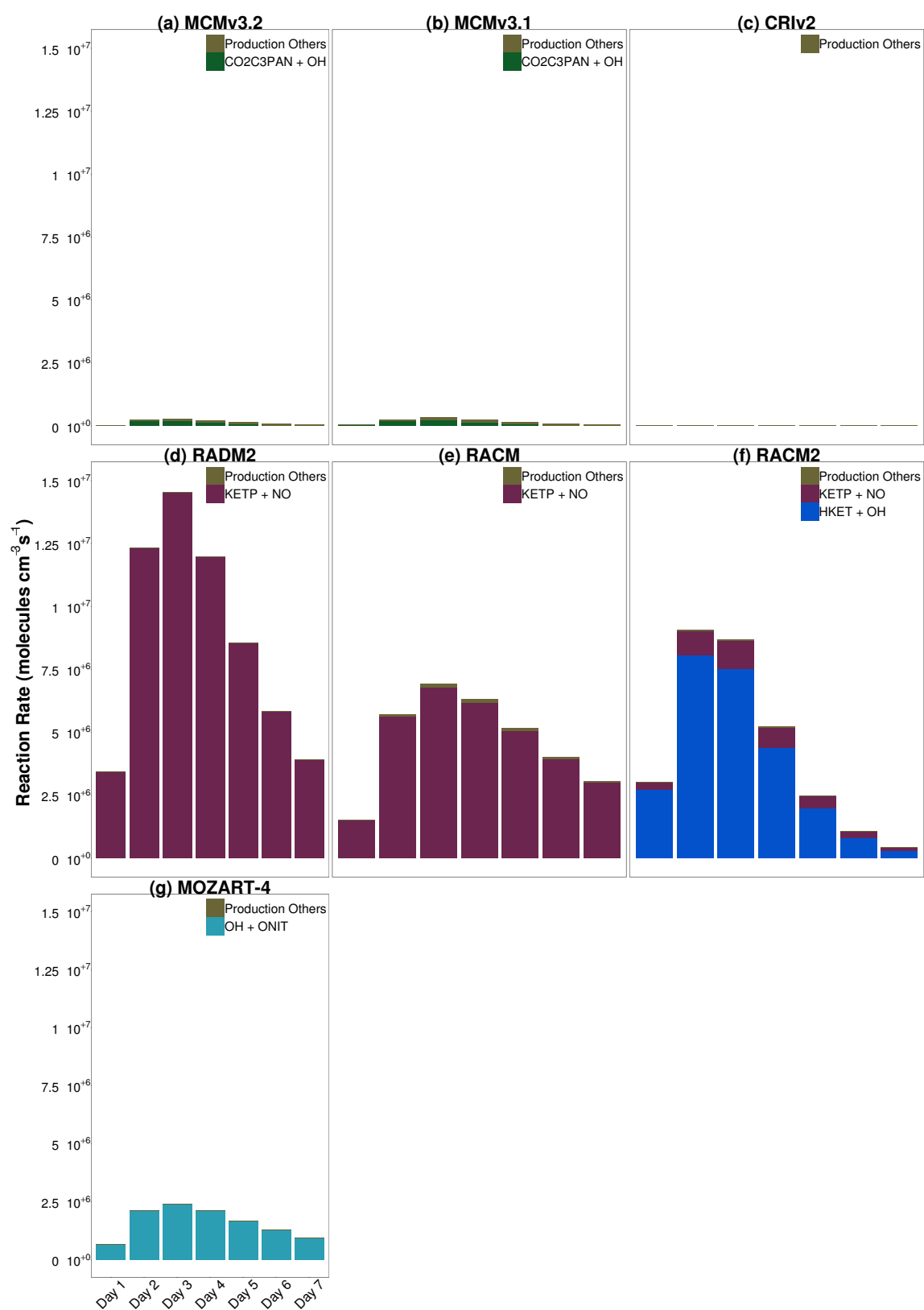


Figure S5: Reactions responsible for day-time methyl glyoxal production during pentane degradation.

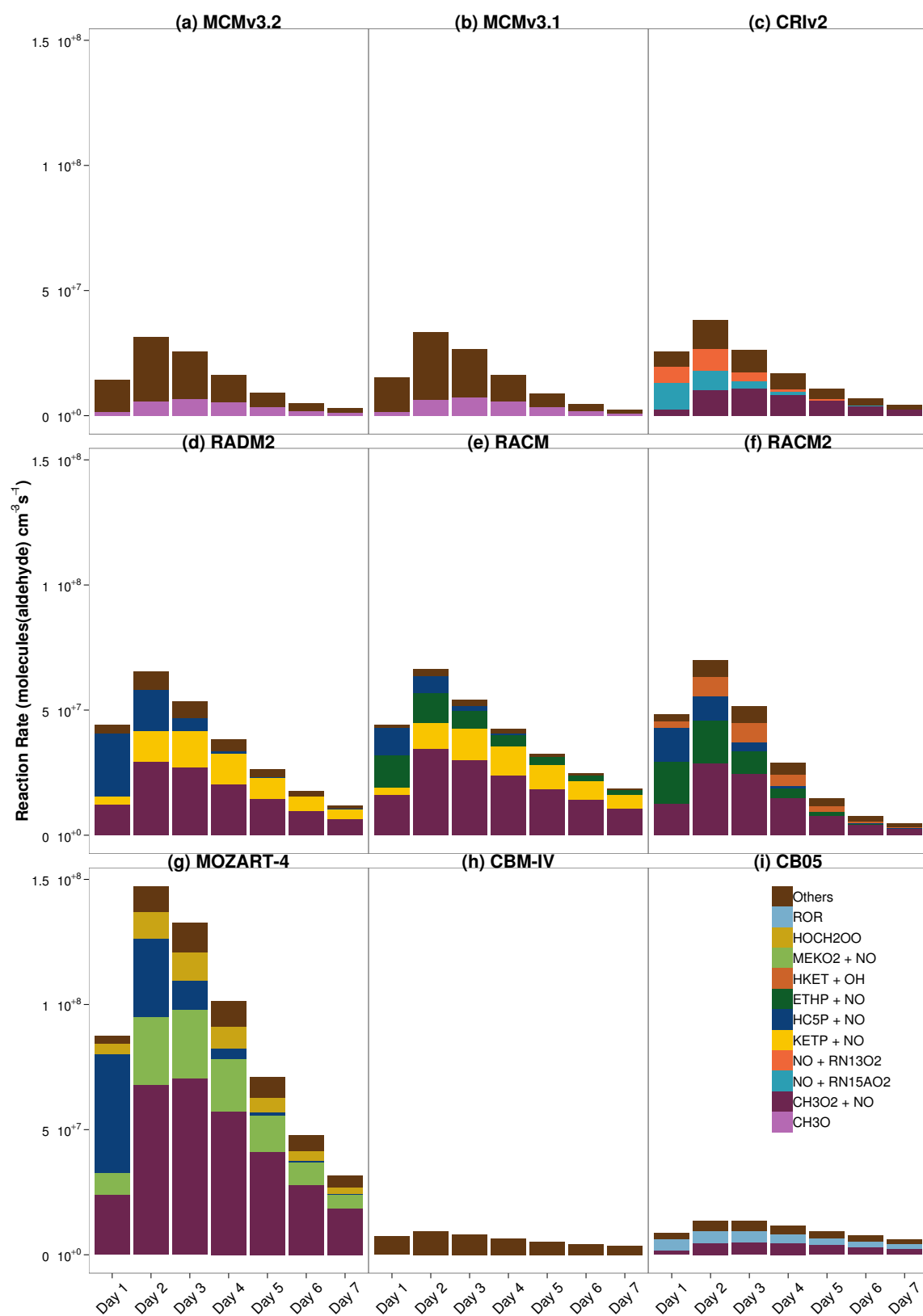


Figure S6: Reactions responsible for day-time total aldehyde production during pentane degradation.

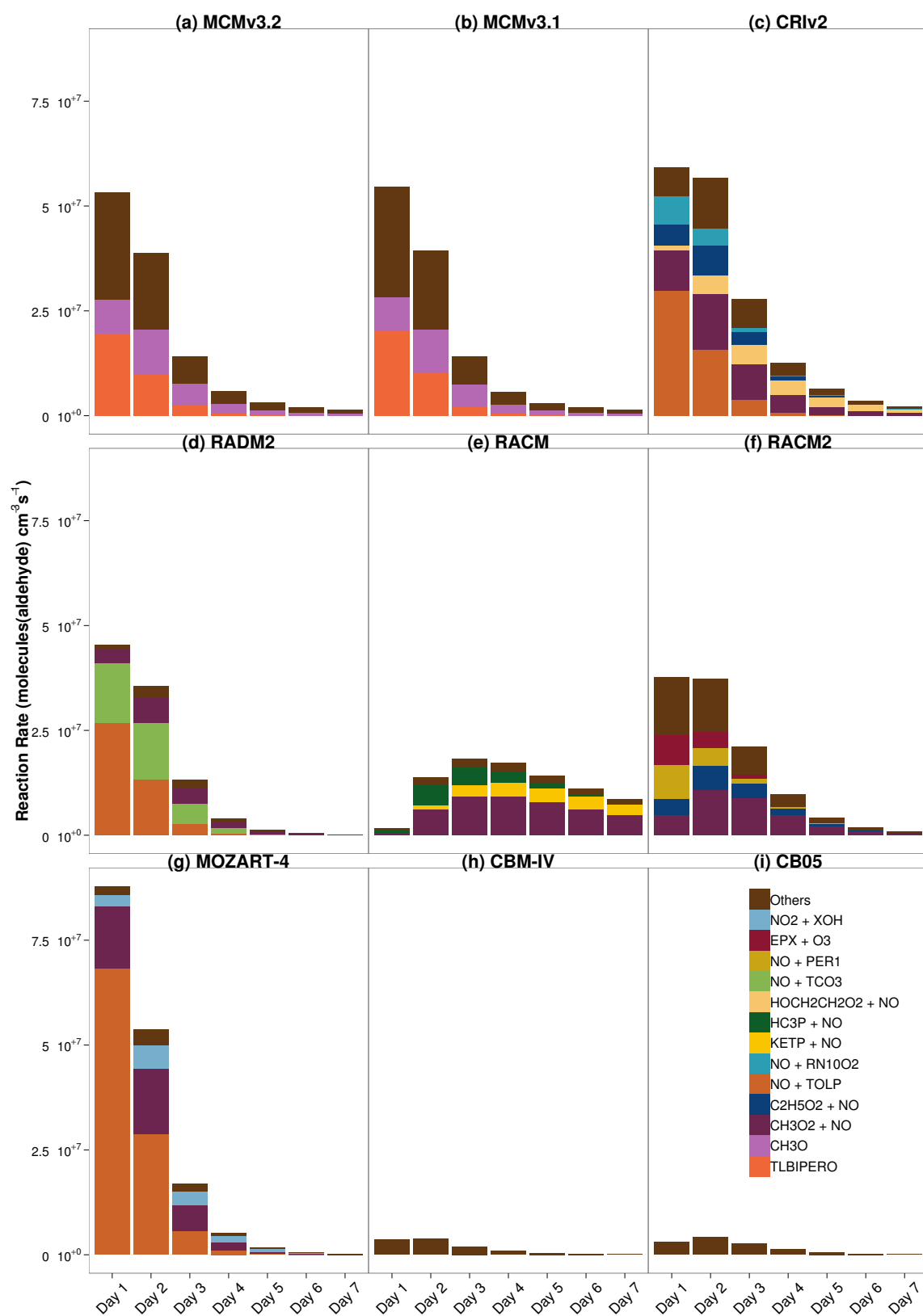


Figure S7: Reactions responsible for day-time total aldehyde production during toluene degradation.

102 References

- Angela K. Baker, Andreas J. Beyersdorf, Lambert A. Doezeema, Aaron Katzenstein, Simone
104 Meinardi, Isobel J. Simpson, Donald R. Blake, and F. Sherwood Rowland. Measurements
of nonmethane hydrocarbons in 28 United States cities. *Atmospheric Environment*, 42:
106 170–182, 2008.
- C. Bloss, V. Wagner, M. E. Jenkin, R. Vollamer, W. J. Bloss, J. D. Lee, D. E. Heard,
108 K. Wirtz, M. Martin-Reviejo, G. Rea, J. C. Wenger, and M. J. Pilling. Development
of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic
110 hydrocarbons. *Atmospheric Chemistry and Physics*, 5:641–664, 2005.
- T. M. Butler, M. G. Lawrence, D. Taraborrelli, and J. Lelieveld. Multi-day ozone
112 production potential of volatile organic compounds calculated with a tagging approach.
Atmospheric Environment, 45(24):4082–4090, 2011.
- V. Damian, A. Sandu, M. Damian, F. Potra, and G.R. Carmichael. The kinetic
114 preprocessor KPP - A software environment for solving chemical kinetics. *Computers
116 and Chemical Engineering*, 26(11):1567–1579, 2002.
- L. K. Emmons, S. Walters, P. G. Hess, J.-F. Lamarque, G. G. Pfister, D. Fillmore,
118 C. Granier, A. Guenther, D. Kinnison, T. Laepple, J. Orlando, X. Tie, G. Tyndall,
C. Wiedinmyer, S. L. Baughcum, and S. Kloster. Description and evaluation of the Model
120 for Ozone and Related chemical Tracers, version 4 (MOZART-4). *Geoscientific Model
Development*, 3:43–67, 2010.
- Michael W. Gery, Gary Z. Whitten, James P. Killus, and Marcia C. Dodge. A
122 photochemical kinetics mechanism for urban and regional scale computer modeling.
124 *Journal of Geophysical Research*, 94(D10):12,925–12,956, 1989.
- Wendy S. Goliff, William R. Stockwell, and Charlene V. Lawson. The regional atmospheric
126 chemistry mechanism, version 2. *Atmospheric Environment*, 68:174–185, 2013.
- M. E. Jenkin, S. M. Saunders, V. Wagner, and M. J. Pilling. Protocol for the development of
128 the Master Chemical Mechanism, MCM v3 (Part B): Tropospheric degradation of aromatic
volatile organic compounds. *Atmospheric Chemistry and Physics*, 3(1):181–193, 2003.

130 M. E. Jenkin, L. A. Watson, S. R. Utembe, and D. E. Shallcross. A Common Representative
Intermediates (CRI) mechanism for VOC degradation. Part 1: Gas phase mechanism
132 development. *Atmospheric Environment*, 42:7185–7195, 2008.

Michael E. Jenkin, Sandra M. Saunders, and Michael J. Pilling. The tropospheric
134 degradation of volatile organic compounds: A protocol for mechanism development.
Atmospheric Environment, 31(1):81–104, 1997.

136 Andrew Rickard, Jenny Young, and Stephen Pascoe. The Master Chemical Mechanism:
Major updates in MCM v3.2. http://mcm.leeds.ac.uk/MCM/project.htm#New_3.2,
138 2014. [Online; accessed 12-November-2014].

R. Sander, A. Kerkweg, P. Jöckel, and J. Lelieveld. Technical Note: The new comprehensive
140 atmospheric chemistry module MECCA. *Atmospheric Chemistry and Physics*, 5:445–450,
2005.

142 S. M. Saunders, M. E. Jenkin, R. G. Derwent, and M. J. Pilling. Protocol for the
development of the Master Chemical Mechanism, MCM v3 (Part A): Tropospheric
144 degradation of non-aromatic volatile organic compounds. *Atmospheric Chemistry and
Physics*, 3(1):161–180, 2003.

146 William R. Stockwell, Paulete Middleton, Julius S. Chang, and Xiaoyan Tang. The Second
Generation Regional Acid Deposition Model Chemical Mechanism for Regional Air Quality
148 Modeling. *Journal of Geophysical Research*, 95(D10):16,343–16,367, 1990.

William R. Stockwell, Frank Kirchner, Michael Kuhn, and Stephan Seefeld. A new
150 mechanism for regional atmospheric chemistry modeling. *Journal of Geophysical Research
D: Atmospheres*, 102(22):25,847–25,879, 1997.

152 Greg Yarwood, Sunja Rao, Mark Yocke, and Gary Z. Whitten. Updates to the Carbon
Bond Chemical Mechanism: CB05. Technical report, U. S Environmental Protection
154 Agency, 2005.