

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

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

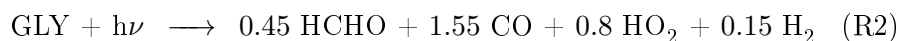
The MCM v3.2 (Jenkin et al., 1997, 2003; Saunders et al., 2003; Bloss et al., 2005; Rickard et al., 2014) was the reference mechanism. Its approach to inorganic chemistry, dry deposition, photolysis and peroxy radical–peroxy radical reactions were applied to all mechanisms.

S2.1 Photolysis

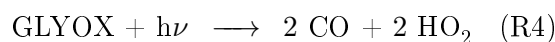
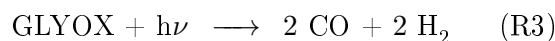
20 Photolysis was parameterised as a function of the solar zenith angle as per the MCM
 approach (Saunders et al., 2003). Species from reduced mechanisms having a direct
 22 MCM v3.2 counterpart were assigned the corresponding MCM v3.2 photolysis rate.
 Otherwise the recommended mechanism rate was used to determine the appropriate MCM
 24 v3.2 photolysis rate. In some cases this was the MCM v3.2 photolysis rate closest in
 magnitude to that specified in the mechanism.

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

30 Photolysis of a reduced mechanism species was sometimes represented by more than
 one MCM v3.2 photolysis reaction. The original mechanism product yields were preserved
 32 using combinations of the MCM v3.2 rates. This approach was used for RADM2 glyoxal
 photolysis. Glyoxal photolysis in RADM2 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 (R1) product yields were retained using a photolysis rate 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 S1 illustrates the product
 40 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

	Rate	MCM v3.2 Product 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 rates retaining RADM2 glyoxyl photolysis product yields.

Mechanism	Reaction	Rate Constant
MCM v3.2	C2H5O2 = C2H5O	$k \cdot \text{RO2} \cdot 0.6 \text{ s}^{-1}$
	C2H5O2 = C2H5OH	$k \cdot \text{RO2} \cdot 0.2 \text{ s}^{-1}$
	C2H5O2 = CH3CHO	$k \cdot \text{RO2} \cdot 0.2 \text{ s}^{-1}$
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	$2 \times 10^{-13} \cdot \text{RO2} \text{ s}^{-1}$

Table S2: Ethyl peroxy radical (C₂H₅O₂) self and cross organic peroxy reactions in the MCM v3.2 and MOZART-4 mechanisms 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	$9.4 \times 10^{-14} \exp(390/T) \cdot \text{RO2} \text{ s}^{-1}$
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	$1.18 \times 10^{-13} \exp(158/T) \cdot \text{RO2} \text{ s}^{-1}$

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

ambiguities when implementing the tagging scheme. Namely, which tag to be used for the
46 products of reactions between RO_2 having different tags. To avoid such ambiguities, the
MCM v3.2 approach to self and cross RO_2 reactions is used – each RO_2 species reacts
48 with the pool of all other RO_2 at a single uniform rate. This was represented as a
pseudo-unimolecular reaction whose rate constant includes a factor ‘RO2’ which was the
50 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
52 two methods. Firstly, by using the $\text{RO}_2 + \text{RO}_2$ reaction and halving the product yields.
This is demonstrated for the MOZART-4 treatment of the ethyl peroxy radical in Table S2.
54 Alternatively, the $\text{RO}_2 + \text{CH}_3\text{O}_2$ reaction was used and the products due to CH_3O_2 were
removed. As an example, Table S3 outlines the steps taken to determine the ETHP
56 pseudo-unimolecular reaction in RACM2.

First the products due to MO_2 , representing CH_3O_2 in RACM2, are determined
58 as outlined above using the $\text{MO}_2 + \text{MO}_2$ reaction. The MO_2 product yields are then
subtracted from the $\text{ETHP} + \text{MO}_2$ reaction. Any products having a negative yield were
60 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
62 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, its
pseudo-unimolecular reaction was derived by subtracting the CH_3O_2 product yields from
64 the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{O}_2$. 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 $\text{CH}_3\text{C}(\text{O})\text{O}_2$.

66 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
68 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 in the atmosphere.

70 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
72 shown in Figure S1.

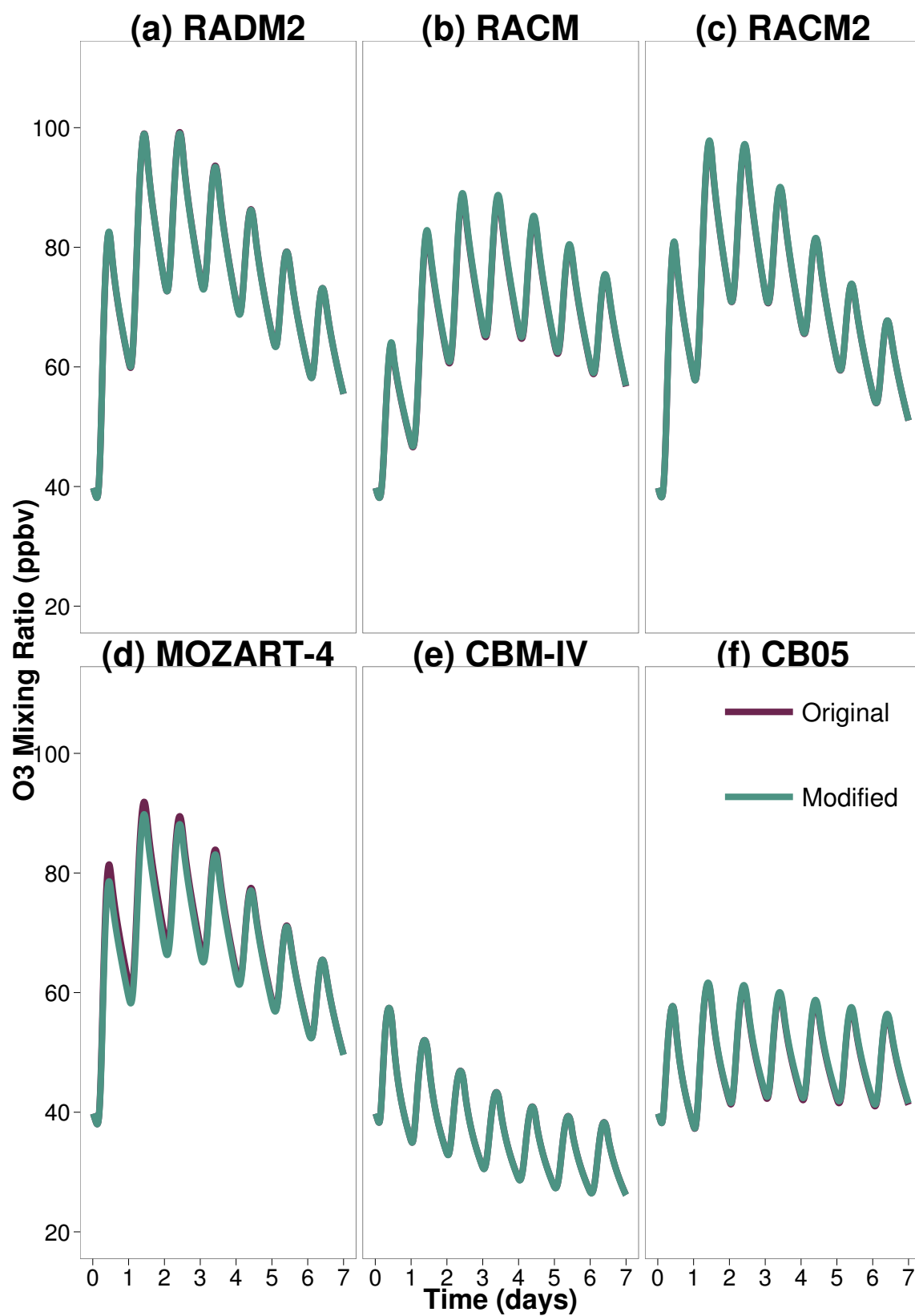


Figure S1: O₃ mixing ratio time series for each reduced mechanism using the original and modified approach to RO₂-RO₂ reactions

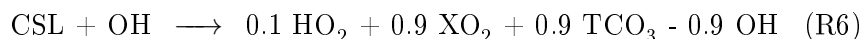
S2.3 Dry Deposition

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

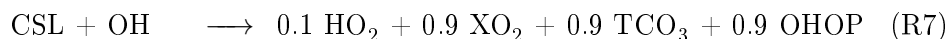
S2.4 Negative Product Yield Treatment

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 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 a ‘NULL’ product.

For example, in RADM2 the OH + cresol (CSL) reaction has negative OH yield (R6).



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



S3 Mapping Emitted NMVOC to Mechanism Species

The emitted NMVOCs are typical of Los Angeles taken from Baker et al. (2008). The MCM v3.2, v3.1 (Jenkin et al., 1997; Saunders et al., 2003; Jenkin et al., 2003) and CRI v2 (Jenkin et al., 2008) have specific species designed to represent each NMVOC explicitly.

NMVOC representation in the other mechanisms required mapping to specific mechanism species. This mapping followed the mechanism references. 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 mechanism species.

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)	ETHA	Ethane
	HC8	OH rate constant (298 K, 1 atm) greater than 6.8×10^{-12} $\text{cm}^3 \text{s}^{-1}$		PAR	Paraffin carbon bond C–C
	ETE	Ethene		OLE	Terminak olefin carbon bond R–C=C
	OLT	Terminal alkenes		FORM	Formaldehyde
	OLI	Internal alkenes		ISOP	Isoprene
	ISO	Isoprene		TOL	Toluene and other monoalkyl aromatics
	TOL	Toluene and less reactive aromatics		XYL	Xylene and other polyalkyl aromatics
	XYL	Xylene and more reactive 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.

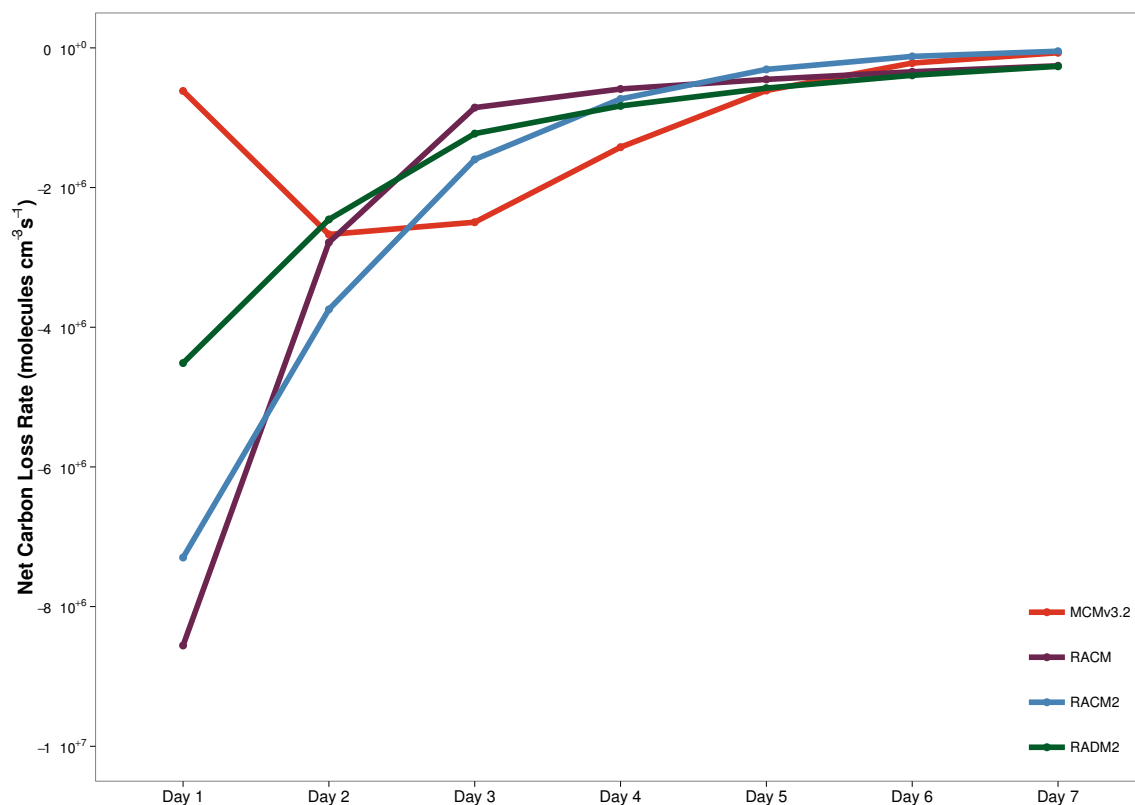


Figure S2: Day-time reactive carbon loss during octane degradation in RADM2, RACM and RACM compared to MCM v3.2.

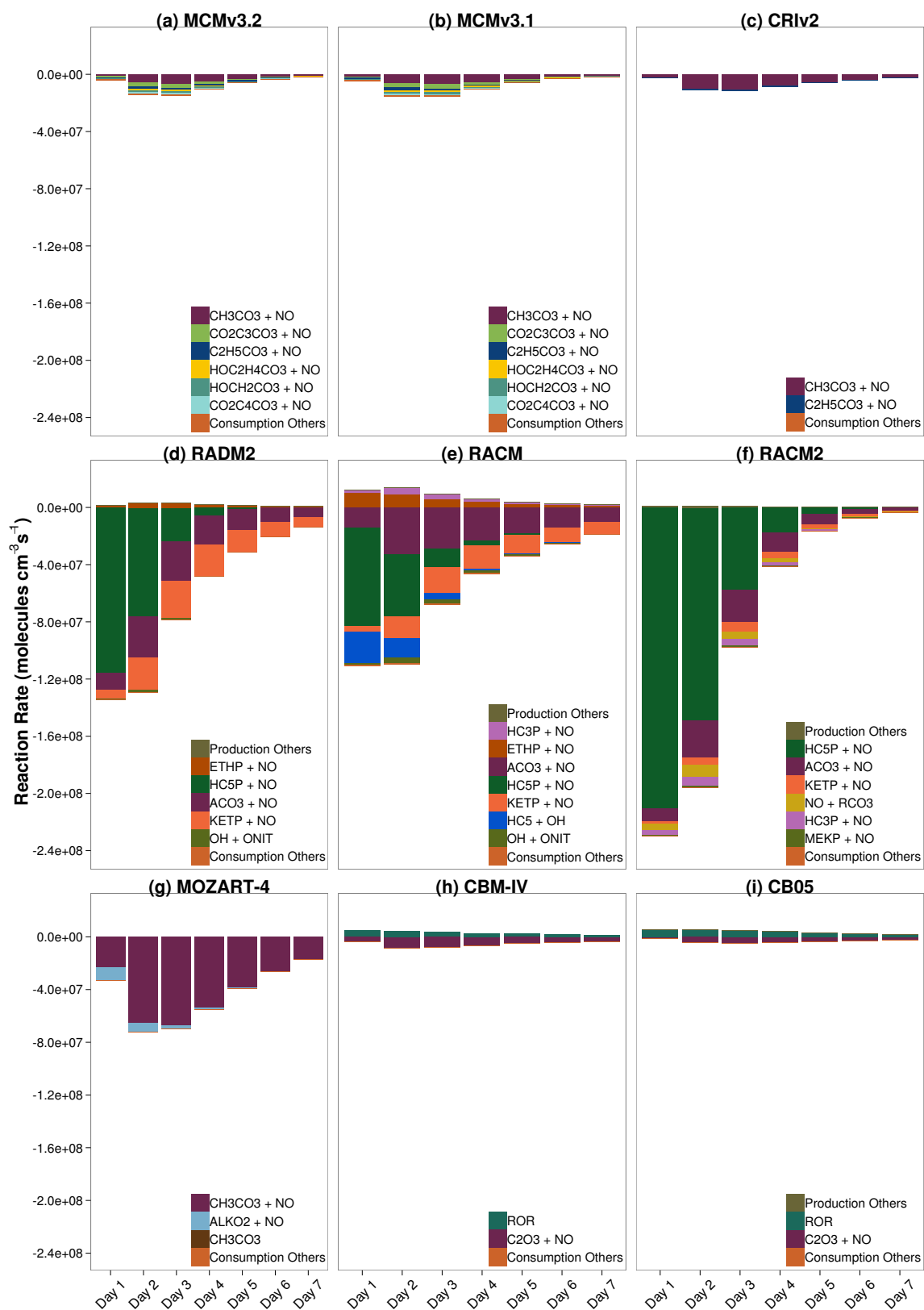


Figure S3: Reactions responsible for day-time reactive carbon loss during pentane degradation.

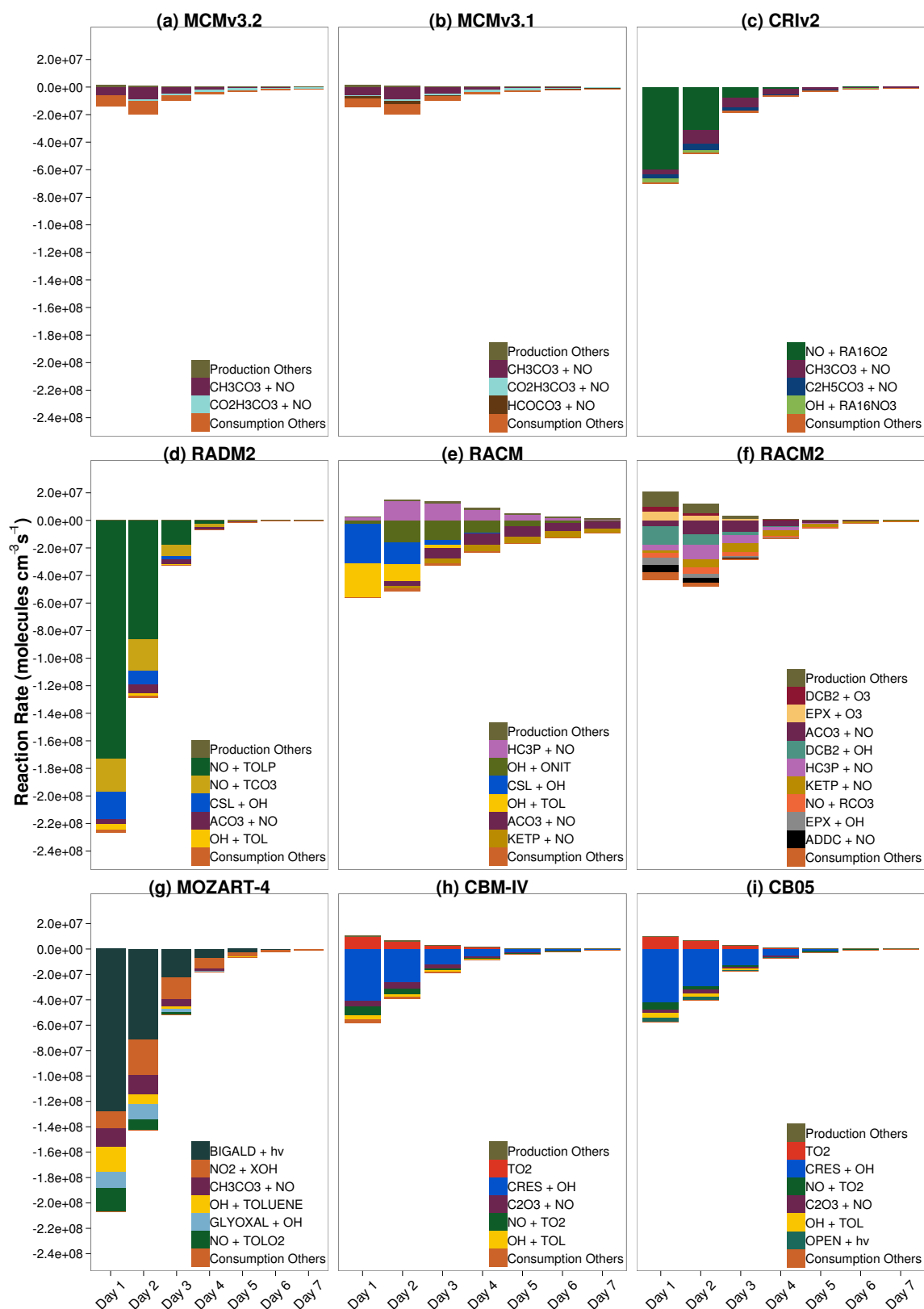


Figure S4: Reactions responsible for day-time reactive carbon loss during toluene degradation.

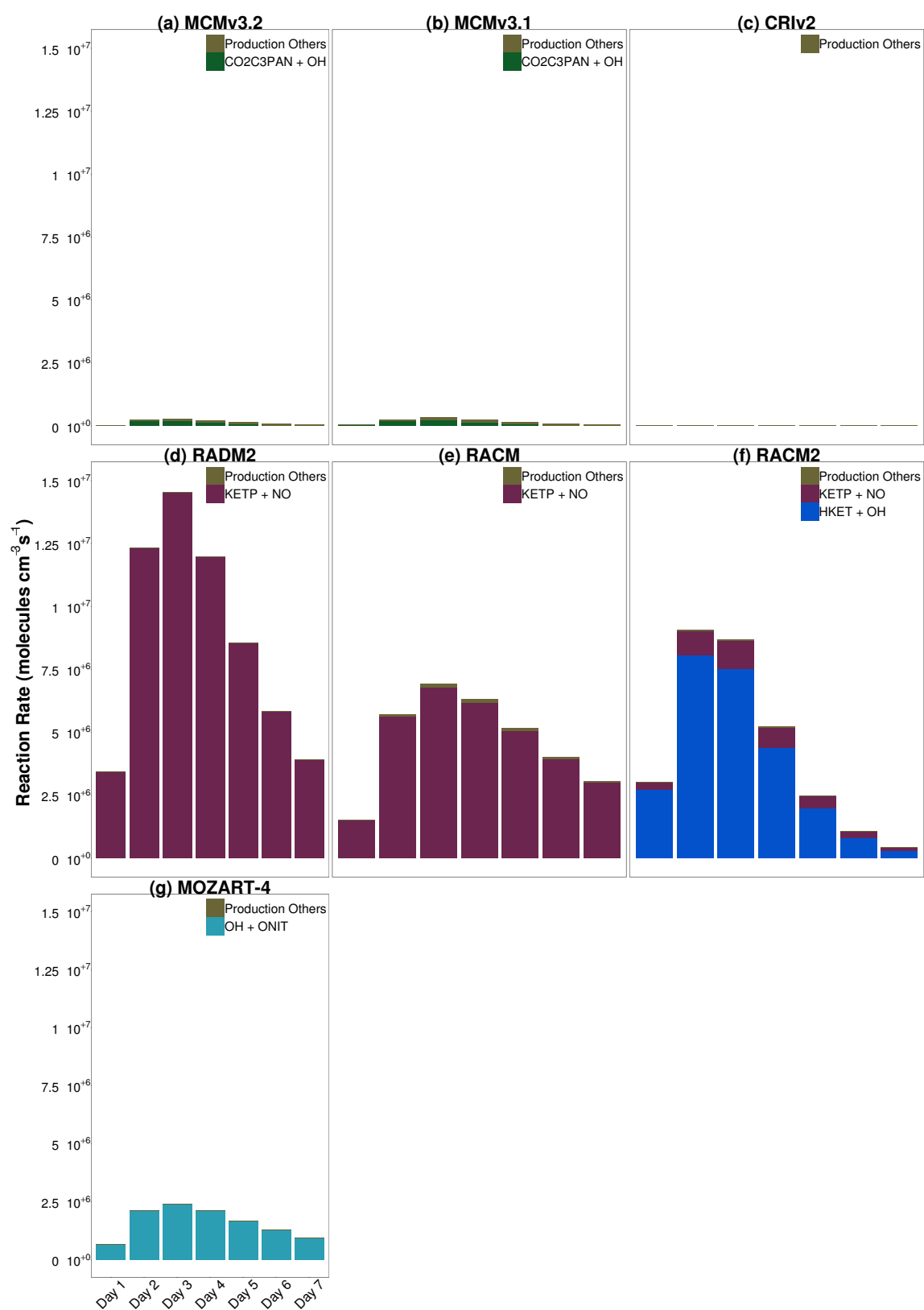


Figure S5: Reactions responsible for day-time methyl glyoxal production during pentane degradation.

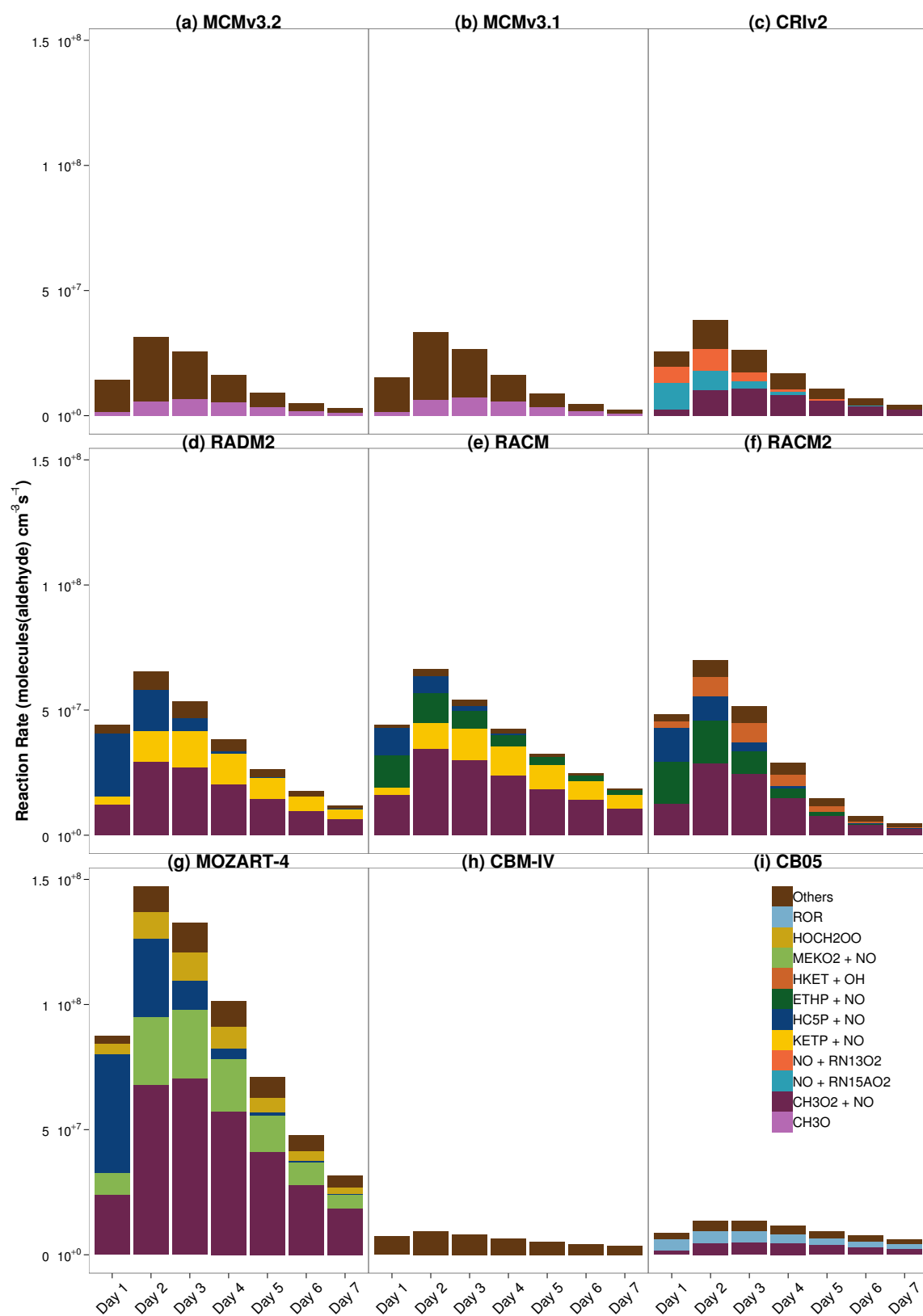


Figure S6: Reactions responsible for day-time total aldehyde production during pentane degradation.

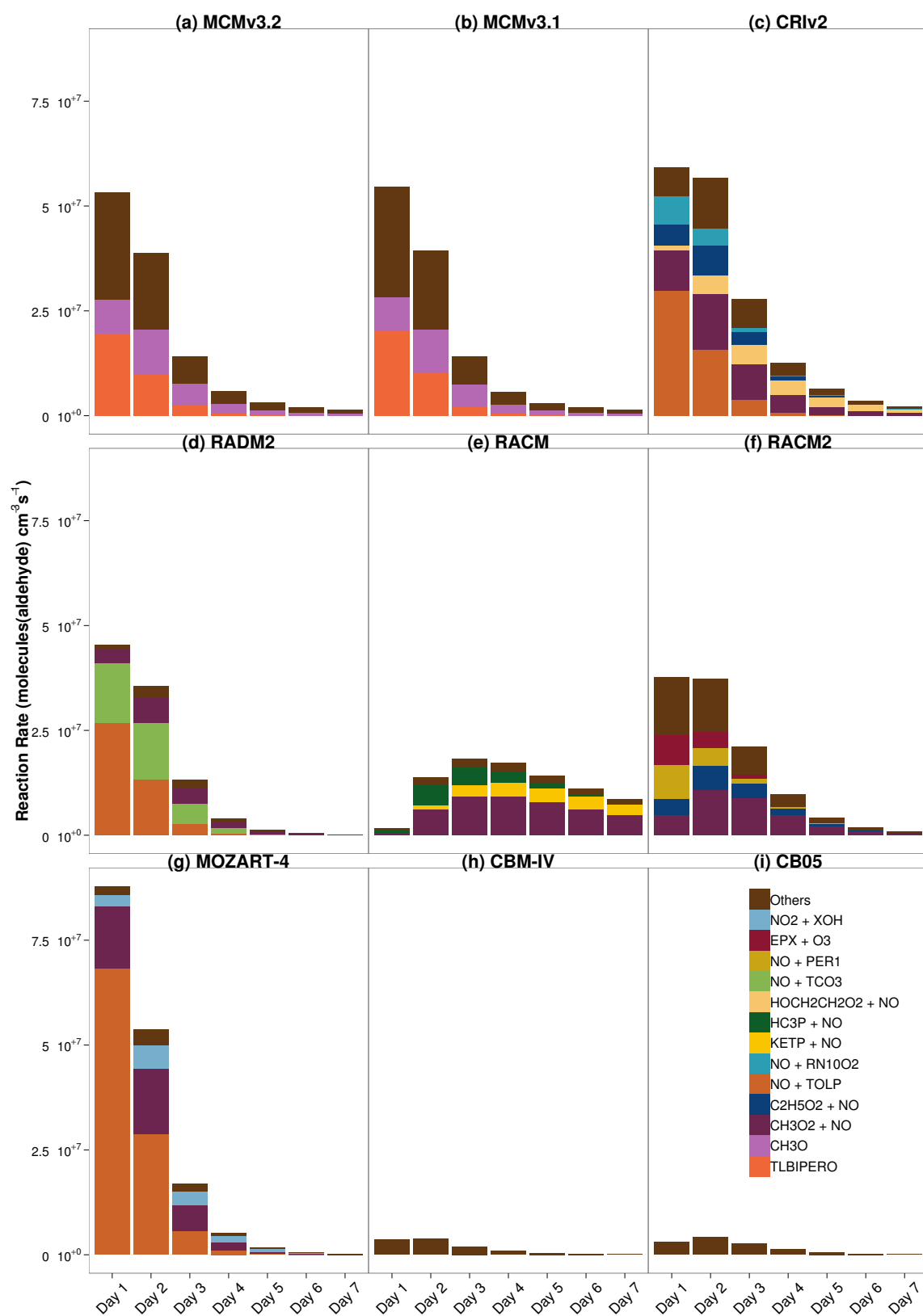


Figure S7: Reactions responsible for day-time total aldehyde production during toluene degradation.

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