

Annex IV: Gas-phase photolysis used in GECKO-A

SI-Table 1: Gas-phase photolysis considered in GECKO-A for various species and functional group surrogates. Photolysis rates are calculated using the TUV model for 40°N and the solar zenith angle of 45°.

Species / functional group	Reference species	General formula (SMILES ^(*))		Typical products	J(s ⁻¹) at SZA=45°
		NO ₂			8.08×10 ⁻³
entire molecule	propenal (acrolein)	C=CC=O	i ii iii	C=CC•=O + HO ₂ C=C• + CO + HO ₂ CC•(OO•)* + CO	5.55×10 ⁻⁷ 4.16×10 ⁻⁷ 4.16×10 ⁻⁷
entire molecule	methacrolein	CC(=C)C=O	i ii iii	C=C•C + CO + HO ₂ CC•(OO•)*C + CO C=C(C)CO• + HO ₂	4.47×10 ⁻⁶ 4.47×10 ⁻⁶ 4.47×10 ⁻⁶
entire molecule	acetone	CC(=O)C		CC=O• + CH ₃ •	3.82×10 ⁻⁷
entire molecule	2,3-butanedione (biacetyl)	CC(=O)C(C)=O		2 CC•=O	2.29×10 ⁻⁴
entire molecule	pyruvic acid	CC(=O)C(O)=O		CC=O + CO ₂	1.03×10 ⁻⁴
entire molecule	methyl vinyl ketone	CC(=O)C=C	i ii	C=CC + CO C=C• + CC•=O	4.29×10 ⁻⁶ 4.29×10 ⁻⁷
entire molecule	methyl glyoxal	CC(=O)C=O	i ii iii	CC•=O + CO + HO ₂ CC=O + CO CH ₄ + 2 CO	7.01×10 ⁻⁵ 3.90×10 ⁻⁶ 3.90×10 ⁻⁶
entire molecule	hydroxyacetone	CC(=O)CO		CC•=O + CH ₂ O + HO ₂	1.51×10 ⁻⁶
entire molecule	3,3-dimethyl butanal	CC(C)(C)CC=O		CC(C)(C)C• + CO + HO ₂	2.58×10 ⁻⁵
entire molecule	t-butyl nitrate	CC(C)(C)O[N](O)=O		CC(C)(C)O• + NO ₂	5.66×10 ⁻⁶
entire molecule	2,4-dimethyl-3-pentanone	CC(C)C(=O)C(C)C		CC(C)C•=O + CC•C	8.30×10 ⁻⁶
entire molecule	i-butanal (i-butyraldehyde)	CC(C)C=O		CC•C + CO + HO ₂	3.80×10 ⁻⁵
entire molecule	4-methyl-2-pentanone	CC(C)CC(C)=O	i ii	C•C(C)C + CC•=O CC(=O)C + C=CC	1.61×10 ⁻⁶ 3.87×10 ⁻⁶

entire molecule	3-methyl butanal	CC(C)CC=O	i	CC(C)C• + CO + HO ₂	1.54×10 ⁻⁵
			ii	C=CC + CC=O	1.05×10 ⁻⁵
entire molecule	5-methyl-2-hexanone	CC(C)CCC(C)=O	i	C•CC(C)C + CC•=O	1.28×10 ⁻⁶
			ii	C=C(C)C + CC(=O)C	3.06×10 ⁻⁶
entire molecule	i-propyl nitrate	CC(C)O[N](O)=O		CC(C)O• + NO ₂	1.93×10 ⁻⁶
entire molecule	butane-2,3-dinitrate	CC(O[N](O)=O)C(C)O[N](O)=O		CC(O•)C(C)O[N](O)=O + NO ₂	7.41×10 ⁻⁶
entire molecule	propane-1,2-dinitrate	CC(O[N](O)=O)CO[N](O)=O	i	CC(O•)CO[N](O)=O + NO ₂	3.68×10 ⁻⁶
			ii	CC(O[N](O)=O)CO• + NO ₂	3.68×10 ⁻⁶
entire molecule	crotonaldehyde	CC=CC=O	i	CC=C• + CO + HO ₂	3.29×10 ⁻⁶
			ii	CC=CCO• + HO ₂	3.29×10 ⁻⁶
			iii	CCC• (OO•)* + CO	3.29×10 ⁻⁶
entire molecule	acetaldehyde	CC=O		CH ₃ • + CO + HO ₂	3.51×10 ⁻⁶
entire molecule	3-pentanone	CCC(=O)CC		CCCO• + CC•	3.07×10 ⁻⁶
entire molecule	2-butanone	CCC(C)=O	i	CC•=O + CC•	2.54×10 ⁻⁶
			ii	CCC•=O + CH ₃ •	4.37×10 ⁻⁷
entire molecule	2-methylbutylnitrate	CCC(C)CO[N](O)=O		CCC(C)CO• + NO ₂	1.70×10 ⁻⁶
entire molecule	butan-2-yl nitrate	CCC(C)O[N](O)=O		CC(O•)CC + NO ₂	1.76×10 ⁻⁶
entire molecule	pentan-3-yl nitrate	CCC(CC)O[N](O)=O		CCC(O•)CC + NO ₂	1.64×10 ⁻⁶
entire molecule	butane-1,2-dinitrate	CCC(O[N](O)=O)CO[N](O)=O	i	CCC(O•)CO[N](O)=O + NO ₂	5.03×10 ⁻⁶
			ii	CCC(O[N](O)=O)CO• + NO ₂	5.03×10 ⁻⁶
entire molecule	propanal	CCC=O		CC• + CO + HO ₂	1.30×10 ⁻⁵
entire molecule	2-pentanone	CCCC(C)=O		CCC• + CC•=O	4.05×10 ⁻⁶
entire molecule	pentan-2-yl nitrate	CCCC(C)O[N](O)=O		CC(O•)CCC + NO ₂	1.69×10 ⁻⁶
entire molecule	butanal	CCCC=O	i	CCC• + CO + HO ₂	8.68×10 ⁻⁶
			ii	C=C + CC=O	2.74×10 ⁻⁶
entire molecule	pentanal	CCCCC=O	i	CCCC• + CO + HO ₂	6.63×10 ⁻⁶
			ii	C=CC + CC=O	9.70×10 ⁻⁶
entire molecule	hexanal	CCCCCC=O	i	CCCCC• + CO + HO ₂	3.55×10 ⁻⁶
			ii	C=CCC + CC=O	8.27×10 ⁻⁶
entire molecule	n-pentyl nitrate	CCCCCO[N](O)=O		CCCCCO• + NO ₂	1.71×10 ⁻⁶

entire molecule	n-butyl nitrate	CCCCO[N](O)=O		CCCCO• + NO ₂	1.71×10 ⁻⁶
entire molecule	propyl nitrate	CCCO[N](O)=O		CCCO• + NO ₂	1.84×10 ⁻⁶
entire molecule	ethyl nitrate	CCO[N](O)=O		CCO• + NO ₂	1.16×10 ⁻⁶
entire molecule	methyl nitrate	CO[N](O)=O		CH3(O•) + NO ₂	7.27×10 ⁻⁷
entire molecule	methyl hydroperoxide	COO		CH3(O•) + HO	4.25×10 ⁻⁶
entire molecule	methyl peroxy nitrate	COO[N](O)=O	i	CH3(OO•) + NO ₂	3.12×10 ⁻⁶
			ii	CH3(O•) + NO ₃	3.12×10 ⁻⁶
entire molecule	but-1-ene-3,4-dinitrate	O[N](=O)OCC(O[N](O)=O)C=C	i	O[N](=O)OCC(O•)C=C + NO ₂	2.23×10 ⁻⁶
			ii	O•CC(O[N](O)=O)C=C + NO ₂	2.23×10 ⁻⁶
entire molecule	but-2-ene-1,4-dinitrate	O[N](=O)OCC=CCO[N](O)=O		O•CC=CCO[N](O)=O + NO ₂	4.39×10 ⁻⁶
entire molecule	2-methyl hexadienedial	O=CC(C)=CC=CC=O	i	O=CC(C)=CC=C• + CO + HO ₂	2.46×10 ⁻⁵
			ii	CC•=CC=CC=O + CO + HO ₂	2.46×10 ⁻⁵
			iii	O=CC(C)=CC=CC•=O + HO ₂	2.46×10 ⁻⁵
			iv	O=C•C(C)=CC=CC=O + HO ₂	2.46×10 ⁻⁵
entire molecule	hexadienedial	O=CC=CC=CC=O	i	C•=CC=CC=O + CO + HO ₂	4.77×10 ⁻⁵
			ii	O=CC=CC=CCO• + HO ₂	4.77×10 ⁻⁵
entire molecule	glyoxal	O=CC=O	i	2 CO + HO ₂	3.44×10 ⁻⁶
			ii	2 CO + 2 HO ₂	2.91×10 ⁻⁵
			iii	CH2O + CO	1.47×10 ⁻⁵
entire molecule	peroxy acetyl nitrate	O=COO[N](O)=O		CC(=O)OO• + NO ₂	6.24×10 ⁻⁷
entire molecule	oxalic acid	OC(=O)C(=O)=O	i	CHO(OH) + CO ₂	3.55×10 ⁻⁷
			ii	CO2 + CO	1.33×10 ⁻⁷
entire molecule	glyoxylic acid	OC(=O)C=O	i	CH2O + CO ₂	1.26×10 ⁻⁴
			ii	CO + CO	1.63×10 ⁻⁵
entire molecule	glycolaldehyde	OCC=O		CH2O + CO + 2 HO ₂	6.82×10 ⁻⁶
entire molecule	nitrooxyethanol	OCCO[N](O)=O		OCCO• + NO ₂	6.00×10 ⁻⁸
entire molecule	hydroxymethylhydroperoxide	OCOO		CH2(O•)(OH) + OH	3.90×10 ⁻⁶

acid, a-keto-	pyruvic acid	$RC(=O)C(=O)O$		$RC(O)=O + CO_2$	1.03×10^{-4}
acid, a-C in epoxide, MCM(**)	methyl vinyl ketone	$RC1OC1C(=O)OO$		$RC \bullet C=O + OH$	4.29×10^{-7}
acid, a-C in epoxide, MCM	methyl vinyl ketone	$RC1OC1C(=O)OO$		$RC \bullet C=O + OH$	4.29×10^{-7}
a-di-ketone	biacetyl	$RC(=O)C(=O)R$		$RC \bullet =O + RC \bullet =O$	2.29×10^{-4}
a-di-ketone with b-hydroxy, MCM	2,3-butanedione (biacetyl)	$RC(=O)C(=O)R$		$RC \bullet =O + R \bullet + CO + HO_2$	2.29×10^{-4}
aldehyde, 2ry a-C in epoxide, MCM	i-butanal (i-butryaldehyde)	$RC1OC1(C)C=O$		Various	3.80×10^{-5}
aldehyde, 2ry unsaturated a-C, b-C, MCM	methacrolein	$R=C(C)C=O$	i ii	$C=C \bullet C + CO + HO_2$ $C=C(C)CO \bullet + HO_2$	4.47×10^{-6} 4.47×10^{-6}
aldehyde, 2ry unsaturated a-C	acrolein	$RC(R)=C(R)C=O$	i ii iii	$RC(R)=C \bullet R + CO + HO_2$ Criegee radical + CO $RC(R)=C(R)C \bullet =O + HO_2$	2.65×10^{-6} 2.57×10^{-6} 2.57×10^{-6}
aldehyde, a-C in epoxide, MCM	butanal	$RC1OC1C=O$		$CCC \bullet + CO + HO_2$	8.68×10^{-6}
aldehyde, a-hydroperoxy-	glycolaldehyde	$RC(OO)(R)C=O$		$RC \bullet (=O)R + CO + 2 HO_2$	6.82×10^{-6}
aldehyde, a-hydroxy-	glycolaldehyde	$RC(O)(R)C=O$		$RC \bullet (=O)R + CO + HO_2 + OH$	6.82×10^{-6}
aldehyde, a-keto-	methyl glyoxal	$RC(=O)C=O$	i ii iii	$RC(=O)OO \bullet + CO + HO_2$ $RC=O + CO$ $R + 2 CO$	7.01×10^{-5} 3.90×10^{-6} 3.90×10^{-6}
aldehyde, g-H, 1/2ry a-C a-C	t-pentanal	$RCC=O$ or $RC(R)C=O$	i ii	$RC \bullet R$ or $RC \bullet + CO + HO_2$ Norrish II 1,4 biradical	6.63×10^{-6} 9.70×10^{-6}
aldehyde, g-H, 3ry a-C	n-pentanal	$RC(R)C=O$	i ii	$RC \bullet (R)R + CO + HO_2$ Norrish II 1,4 biradical	4.69×10^{-6} 6.14×10^{-6}
aldehyde, no g-H, 1ry a-C	propanal	$RCC=O$		$RC \bullet + CO + HO_2$	1.30×10^{-5}
aldehyde, no g-H, 2ry a-C	i-butanal (i-butryaldehyde)	$RC(R)C=O$		$RC \bullet R + CO + HO_2$	3.80×10^{-5}
aldehyde, no g-H, 3ry a-C	t-pentanal	$RC(R)(R)C=O$		$RC \bullet (R)R + CO + HO_2$	2.58×10^{-5}
a-unsaturated g-di-aldehyde	trans-butenedial	$RC(C=O)=C(R)C(=O)$	i	$O=C1OCC=C1 + xC$	4.69×10^{-4}
a-unsaturated g-di-aldehyde	butenedial		ii	$O=C1OC(=O)C=C1 + 2 HO_2 + xC$	4.69×10^{-4}

a-unsaturated g-di-ketone	3-hexene-2,5-dione	$RC(=O)C(R)=C(R)C(=O)R$	i	$RC(=O)C=C(R)C\bullet=O + R\bullet$	4.04×10^{-4}
a-unsaturated g-di-ketone			ii	$O=C1OC(=O)C=C1 + xR$	4.04×10^{-4}
a-unsaturated g-keto-aldehyde	4-oxo-2-pentenal	$RC(=O)C(R)=C(R)C(=O)$	i	$CC1=CC(=O)OC1 + xC$	6.38×10^{-4}
			ii	$O=C1OC(=O)C=C1 + R\bullet + 2HO_2 + xC$	6.38×10^{-4}
a-unsaturated ketone	methyl vinyl ketone	$RC=CC(=O)C$	i	$RC=CC + CO$	4.29×10^{-6}
a-unsaturated ketone			ii	$RC=C\bullet + CC\bullet=O$	4.29×10^{-7}
ketone (various), MCM	2-butanone	$RC(=O)R$		various products	2.54×10^{-6}
ketone, a-hydroxy-	hydroxyacetone	$RC(=O)C(O)R$		$RC\bullet=O + RC\bullet O$	2.51×10^{-6}
ketone, no g-H, 2x2/3ry a-C	2,4-dimethyl pentanone	$RC(R)C(=O)C(R)R$		$RC(R)C\bullet=O + C\bullet(R)R$	8.30×10^{-6}
ketone, no g-H, 1ry + 2/3ry a-C	3-pentanone, 2,4-dimethyl pentanone	$RC(R)C(=O)R$		$RC(R)C\bullet=O + R\bullet$	5.69×10^{-6}
ketone, no g-H, 2x1ry a-C	3-pentanone	$RC(=O)R$		$RC\bullet=O + R\bullet$	3.07×10^{-6}
ketone, g-H, 2x2/3ry a-C	2,4-dimethyl pentanone	$RC(R)C(=O)C(R)R$	i	$RC(R)C\bullet=O + C\bullet(R)R$	2.44×10^{-6}
			ii	Norrish II 1,4 biradical	5.86×10^{-6}
ketone, g-H, 1ry + 2/3ry a-C	3-pentanone, 2,4-dimethyl pentanone	$RC(R)C(=O)R$	i	$RC(R)C\bullet=O + R\bullet$	1.67×10^{-6}
			ii	Norrish II 1,4 biradical	4.02×10^{-6}
ketone, with g-H, 2x1ry a-C	3-pentanone	$RC(=O)R$	i	$RC\bullet=O + R\bullet$	9.04×10^{-7}
			ii	Norrish II 1,4 biradical	2.17×10^f
nitrate, 1ry a-C	n-pentyl nitrate	$RCO[N](O)=O$		$RCO\bullet + NO_2$	1.71×10^{-6}
nitrate, 1ry a-C, MCM	propyl nitrate	$RCO[N](O)=O$		$RCO\bullet + NO_2$	1.84×10^{-6}
nitrate, 2ry a-C	2-butyl nitrate	$RC(R)O[N](O)=O$		$RC(R)O\bullet + NO_2$	1.76×10^{-6}
nitrate, 2ry a-C, MCM	i-propyl nitrate	$RC(R)O[N](O)=O$		$RC(R)O\bullet + NO_2 (+ OH)$	1.93×10^{-6}
nitrate, 3ry a-C	t-butyl nitrate	$RC(R)(R)O[N](O)=O$		$RC(R)(R)O\bullet + NO_2$	5.66×10^{-6}
PAN	peroxy acetyl nitrate (PAN)	$RC(=O)OO[N](O)=O$		$RC\bullet=O + NO_2$	6.24×10^{-7}
PAN, a-keto-	methyl glyoxal	$RC(=O)C(=O)OO[N](O)=O$		$RC\bullet=O + CO + NO_2$	7.01×10^{-5}

Notation:

(*) SMILES formulae are used for species with more than 1 carbon, and are arranged according to the Unique SMILES format accessed online at: <http://cactus.nci.nih.gov/translate/> (last access on 28 January 2015)

(**) MCM: photolysis rate assignments are made according to the MCM (Master Chemical Mechanism from Leeds)

33 (other) Notation '1ry,2ry,3ry' ignores the carbon in the main functional group
34 1/2ry means primary or secondary
35 2x2/3ry means that two 2ry or 3ry carbons are attached to the alpha-carbon
36 γ -H describes an abstractable hydrogen, 3 carbons away from the main functional group.
37 α -C denotes the carbon alpha (adjacent) to the main functional group
38 α -(group) describes a functional group attached to the alpha-carbon
39 xC is a counter for 'lost carbon', that is, products with unknown fate.
40