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

Table S1: 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	C=CC•=O + HO_2	5.55×10^{-7}
			ii	C=C• + CO + HO_2	4.16×10^{-7}
			iii	CC•(OO•)* + CO	4.16×10^{-7}
entire molecule	methacrolein	CC(=C)C=O	i	C=C•C + CO + HO_2	4.47×10^{-6}
			ii	CC•(OO•)*C + CO	4.47×10^{-6}
			iii	C=C(C)CO• + HO_2	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	C=CC + CO	4.29×10^{-6}
			ii	C=C• + CC•=O	4.29×10^{-7}
entire molecule	methyl glyoxal	CC(=O)C=O	i	CC•=O + CO + HO_2	7.01×10^{-5}
			ii	CC=O + CO	3.90×10^{-6}
			iii	CH_4 + 2 CO	3.90×10^{-6}
entire molecule	hydroxyacetone	CC(=O)CO		CC•=O + CH2O + 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-butryaldehyde)	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	C•C(C)C + CC•=O	1.61×10^{-6}
			ii	CC(=O)C + C=CC	3.87×10^{-6}

entire molecule	3-methyl butanal	CC(C)CC=O	i ii	CC(C)C• + CO + HO_2 C=CC + CC=O	1.54×10^{-5} 1.05×10^{-5}
entire molecule	5-methyl-2-hexanone	CC(C)CCC(C)=O	i ii	C•CC(C)C + CC•=O C=C(C)C + CC(=O)C	1.28×10^{-6} 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 ii	CC(O•)CO[N](O)=O + NO_2 CC(O[N](O)=O)CO• + NO_2	3.68×10^{-6} 3.68×10^{-6}
entire molecule	crotonaldehyde	CC=CC=O	i ii iii	CC=C• + CO + HO_2 CC=CCO• + HO_2 CCC• (OO•)* + CO	3.29×10^{-6} 3.29×10^{-6} 3.29×10^{-6}
entire molecule	acetaldehyde	CC=O		CH3• + 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 ii	CC•=O + CC• CCC•=O + CH_3•	2.54×10^{-6} 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 ii	CCC(O•)CO[N](O)=O + NO_2 CCC(O[N](O)=O)CO• + NO_2	5.03×10^{-6} 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 ii	CCC• + CO + HO_2 C=C + CC=O	8.68×10^{-6} 2.74×10^{-6}
entire molecule	pentanal	CCCCC=O	i ii	CCCC• + CO + HO_2 C=CC + CC=O	6.63×10^{-6} 9.70×10^{-6}
entire molecule	hexanal	CCCCCC=O	i ii	CCCCC• + CO + HO_2 C=CCC + CC=O	3.55×10^{-6} 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(OO)=O		RC(O)=O + CO_2	1.03×10^{-4}
acid,a-C in epoxide, MCM(**)	methyl vinyl ketone	RC1OC1C(=O)OO		RC•C=O + OH	4.29×10^{-7}
acid,a-C in epoxide, MCM	methyl vinyl ketone	RC1OC1C(=O)OO		RC•C=O + OH	4.29×10^{-7}
a-di-ketone	biacetyl	RC(=O)C(=O)R		RC•=O + RC•=O	2.29×10^{-4}
a-di-ketone with b-hydroxy, MCM	2,3-butanedione (biacetyl)	RC(=O)C(=O)R		RC•=O + R• + 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•C + CO + HO_2 C=C(C)CO• + 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•R + CO + HO_2 Criegge radical + CO RC(R)=C(R)C•=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• + CO + HO_2	8.68×10^{-6}
aldehyde, a-hydroperoxy-	glycolaldehyde	RC(OO)(R)C=O		RC• (=O)R + CO + 2 HO_2	6.82×10^{-6}
aldehyde, a-hydroxy-	glycolaldehyde	RC(O)(R)C=O		RC• (=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• + 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•R or RC• + 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•(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• + CO + HO_2	1.30×10^{-5}
aldehyde, no g-H, 2ry a-C	i-butanal (i-butryaldehyde)	RC(R)C=O		RC•R + CO + HO_2	3.80×10^{-5}
aldehyde, no g-H, 3ry a-C	t-pentanal	RC(R)(R)C=O		RC•(R)R + CO + HO_2	2.58×10^{-5}
a-unsaturated g-di-aldehyde a-unsaturated g-di-aldehyde	trans-butenedial butenedial	RC(C=O)=C(R)C(=O)	i ii	O=C1OCC=C1 + xC O=C1OC(=O)C=C1 + 2 HO_2 + xC	4.69×10^{-4} 4.69×10^{-4}

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

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