On the Photochemistry of Methane and Ethane in the Martian Atmosphere: Towards Indirect Detection of Methane Emissions

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Abstract

We develop an existing 1-D photochemistry model to include a comprehensive description of organic chemistry on Mars that includes the oxidation products of methane (CH\$_4\$) and ethane (C\$_2\$H\$_6\$), a longer-chain hydrocarbon that can be used to differentiate between abiotic and biotic surface releases of CH\$_4\$. We find that CH\$_4\$ is most volatile between 20–50 km during Mars' northern summer, where the local atmospheric CH\$_4\$ lifetime lowers to 25–60 years. We study atmospheric formaldehyde (HCHO) and formic acid (HCOOH), as the two common oxidation products of CH\$_4\$ and C\$_2\$H\$_6\$, and acetaldehyde (CH\$_3\$CHO) and acetic acid (CH\$_3\$COOH) as unique products of C\$_2\$H\$_6\$. We focus our analysis of these gases at Mars' aphelion and perihelion at latitudes between -30\$^{\circ}\$ and 30\$^{\circ}\$, altitudes from the surface to 70 km, and from a homogeonous initial condition of 50 pptv of CH\$_4\$ and C\$_2\$H\$_6\$. From this initial condition, CH\$_4\$ produces HCHO in a latitude-independent layered structure centred at 20–30 km at aphelion with column-averaged mixing ratios of $10\$^{-}{-4}$ pptv, and oxidation of C\$_2\$H\$_6\$ produces HCHO at $10\$^{-}{-2}$ pptv. Formic acid has an atmospheric lifetime spanning 1–10 sols below 10 km that shows little temporal or zonal variability, and is produced in comparable abundances $(10\$^{-}{-3}\$$ pptv) by the oxidation of C\$_2\$H\$_6\$ and CH\$_4\$. We also find that oxidation of 50 pptv of C\$_2\$H\$_6\$ results in $10\$^{-}{-3}\$$ pptv of CH\$_3\$CHO and $10\$^{-}{-4}\$$ pptv of CH\$_3\$CHO results in $10\$^{-}{-4}\$$ pptv of atmospheric CH\$_4\$, potentially representing a new atmospheric source of Martian CH\$_4\$.

Photochemistry of Methane and Ethane in the Martian Atmosphere

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6	Key	Points:
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7	•	Formaldehyde and formic acid are two key photochemical products of CH_4 and
8		$C_2H_6.$
9	•	Oxidation of C_2H_6 produces distinct profiles of acetaldehyde.
10	•	Photolysis of acetaldehyde, produced by C_2H_6 photochemistry, is a source of at-

• Photolysis of acetaldehyde, produced by C₂H₆ photochemistry, is a source of atmospheric CH₄.

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12 Abstract

We develop an existing 1-D photochemistry model to include a comprehensive descrip-13 tion of organic chemistry on Mars that includes the oxidation products of methane (CH_4) 14 and ethane (C_2H_6) , a longer-chain hydrocarbon that can be used to differentiate between 15 abiotic and biotic surface releases of CH_4 . We find that CH_4 is most volatile between 16 20-50 km during Mars' northern summer, where the local atmospheric CH₄ lifetime low-17 ers to 25–60 years. We study atmospheric formaldehyde (HCHO) and formic acid (HCOOH), 18 as the two common oxidation products of CH_4 and C_2H_6 , and acetaldehyde (CH_3CHO) 19 and acetic acid (CH_3COOH) as unique products of C_2H_6 . We focus our analysis of these 20 gases at Mars' aphelion and perihelion at latitudes between -30° and 30° , altitudes from 21 the surface to 70 km, and from a homogeonous initial condition of 50 pptv of CH_4 and 22 C_2H_6 . From this initial condition, CH_4 produces HCHO in a latitude-independent lay-23 ered structure centred at 20–30 km at aphelion with column-averaged mixing ratios of 24 10^{-4} pptv, and oxidation of C₂H₆ produces HCHO at 10^{-2} pptv. Formic acid has an 25 atmospheric lifetime spanning 1–10 sols below 10 km that shows little temporal or zonal 26 variability, and is produced in comparable abundances (10^{-5} pptv) by the oxidation of 27 C_2H_6 and CH_4 . We also find that oxidation of 50 pptv of C_2H_6 results in 10^{-3} pptv of 28 CH_3CHO and 10^{-4} pptv of CH_3COOH . Subsequent UV photolysis of this CH_3CHO re-29 sults in 10^{-4} pptv of atmospheric CH₄, potentially representing a new atmospheric source 30 of Martian CH₄. 31

³² Plain Language Summary

Reports of atmospheric methane (CH_4) on Mars, a potential biosignature, have been 33 made via ground-based telescopes, the Mars Express orbiter, and the Curiosity Rover. 34 However, atmospheric CH_4 has been not observed by all instruments, including the re-35 cently launched ExoMars Trace Gas Orbiter. Reconciling these different measurements 36 of the Martian atmosphere with photochemical model calculations remains a challenge, 37 implying that models are missing a CH₄ loss process and/or there are uncharacterised 38 errors in the data. Here we use a photochemical model of CH_4 and ethane (C_2H_6) and 39 their oxidation products, many of which can now be observed from orbiting satellites, 40 to help reconcile models and data. Using this model, we show that UV photolysis of ac-41 etaldehyde, an oxidation product of C_2H_6 , is a small but potentially significant source 42 of atmospheric CH₄. 43

44 1 Introduction

There is considerable debate in the community about the validity and robustness 45 of detections of atmospheric methane (CH_4) on Mars. Detections and non-detections of 46 atmospheric CH_4 have been reported using data collected by satellites (Formisano et al., 47 2004; Geminale et al., 2011; Fonti & Marzo, 2010; Geminale et al., 2008; Giuranna et 48 al., 2019), Earth-based telescopes (Mumma et al., 2009; Villanueva et al., 2013; Krasnopol-49 sky, 2012; V. A. Krasnopolsky, 2007; Krasnopolsky, 2011; Krasnopolsky et al., 2004; V. Krasnopol-50 sky et al., 1997) and *in situ* instruments (Webster et al., 2018, 2015; Moores et al., 2019). 51 This debate highlights the difficulty of measuring atmospheric CH_4 on Mars, and the gaps 52 in our current understanding of the production and loss terms that determine atmospheric 53 CH_4 on Mars. We explore how the presence of CH_4 could be determined by its oxida-54 tion products and in the process discuss how abiotic CH_4 could be potentially produced 55 by organic chemistry. 56

⁵⁷ Detections of atmospheric CH_4 at the Gale crater by the NASA Curiosity Rover ⁵⁸ were observed episodically rising from mean volume mixing ratios (VMRs) of 0.69 ± 0.25 ⁵⁹ parts per billion (ppbv) to 7.20 ± 2.10 ppbv across a 60-sol period (Webster et al., 2015). ⁶⁰ The diurnal variations of CH_4 observations via Curiosity have recently been substanti-⁶¹ ated by the ExoMars Trace Gas Orbiter's Nadir and Occultation for Mars Discovery (NO- MAD) spectrometer and Atmospheric Chemistry Suite (ACS) (Moores et al., 2019; Korablev et al., 2019). These recent measurements by NOMAD and ACS constrain the upper limit of CH_4 in the Martian atmosphere to 0.05 ppbv.

Ground-based telescopes reported a signal of a plume that contained approximately 65 19,000 tonnes of CH₄ (Mumma et al., 2009) near the Syrtis Major region during Mars' 66 northern hemisphere's midsummer, consistent with an estimated 0.60 kg m $^{-2}$ s⁻¹ sea-67 sonal point source of organic compounds. Other searches for CH_4 on Mars have conversely 68 failed to detect the compound (Webster et al., 2013), including the Trace Gas Orbiter's 69 70 year and a half long search (Korablev et al., 2019). This highlights the possibility of methane being significantly more temporally variable than current models predict (Lefèvre & For-71 get, 2009). This inconsistency with regards to CH₄'s detection has also ignited some polemic 72 against the existance of the gas on Mars (Zahnle et al., 2011). Recent analysis of data 73 from the Planetary Fourier Spectrometer (PFS) aboard the Mars Express orbiter iden-74 tified the presence of CH_4 in the Martian atmosphere that was confirmed via indepen-75 dent observations by Giuranna et al. (2019). These results appear to confirm Curiosity's 76 detection of CH₄ at the Gale Crater. The team retrieved column integrated VMRs of 77 15.5 ± 2.50 ppbv above the Gale Crater only 1 Martian day (sol) after the Curiosity rover's 78 measurement of a 5.78 ± 2.27 ppbv (Webster et al., 2015). 79

To further study these possible emissions of CH_4 , and to also provide a more de-80 tailed series of observations of the vertical structure and composition of Mars' atmosphere, 81 the ExoMars mission program was established by the European Space Agency (ESA) 82 (Vago et al., 2015) and the Russian Roscosmos State Corporation for Space Activities. 83 The first mission conducted within this program was the launch of the Trace Gas Or-84 biter (TGO) in 2016, that included two suites of spectrometers, the Nadir and Occul-85 tation for MArs Discovery (NOMAD) spectrometer (Vandaele et al., 2018) and the At-86 mospheric Chemistry Suite (ACS) (Korablev et al., 2017). The TGO underwent 11 months 87 of aerobraking to reduce its orbital speed and altitude, eventually establishing an approx-88 imately circular orbit of altitude roughly 400 km allowing scientific observations to start 89 in April 2018 (Vandaele et al., 2019). Over the first year, no successful observations of 90 CH_4 were reported by the TGO instrumentation (Korablev et al., 2019). We developed 91 our investigation bearing in mind the capabilities of TGO instruments, especially the so-92 lar occultation channels of NOMAD (NOMAD-SO) and ACS (ACS-MIR). The NOMAD-93 SO instrument has been designed to be sensitive to CH_4 abundances as low as 0.025 ppbv 94 when observed in solar occultation mode (Robert et al., 2016). This expected detection 95 limit was compared to the experimental values in (Vandaele et al., 2019). The TGO in-96 struments improved the experimental upper limit of previous instrumentation to reach 97 a limit of roughly 0.05 ppbv for methane. A few profiles reported in Korablev et al. (2019) 98 and obtained via ACS-MIR, measured in clear northern conditions, were able to achieve qq the most precise detection limits of 0.012 ppby down to an altitude of roughly 3 km. 100

Previous studies using 1-D photochemical models (Wong et al., 2003; Summers et 101 al., 2002) calculate the photochemical lifetime of CH_4 to be roughly 300 years below 70 km. 102 In the absence of a strong surface loss process, surface emissions of CH_4 will then be-103 come homogeneously distributed across the planet after being introduced into the at-104 mosphere. This inconsistency between models and data means that the available atmo-105 spheric data is misinterpreted, and/or there is a loss mechanism that we do no not cur-106 rently consider in models (V. A. Krasnopolsky, 2006). Previous calculations using a global 107 3-D general circulation model have determined that to reconcile models and data we need 108 a CH_4 loss process that is up to 600 times faster than any known process (Lefèvre & For-109 get, 2009). That additional sink would lower the atmospheric lifetime of CH_4 from cen-110 turies to less than 200 days. With the advent of the TGO, another approach we can take 111 is to analyse observed spatial and temporal variations of the oxidation products of at-112 mospheric CH_4 . 113

In this study, we describe the development of the 1-D photochemistry submodule 114 from the LMD-UK General Circulation Model (GCM) (Forget et al., 1999; Lewis et al., 115 1999) to include organic chemistry and run it as an independent model to study pho-116 tochemistry on Mars. We report results from a series of numerical experiments that de-117 scribe how the presence of CH₄ affects photochemistry on Mars. We also report photo-118 chemical results when we replace CH_4 with ethane (C_2H_6) to show this longer-chain hy-119 drocarbon produced richer atmospheric chemistry but also allows us to consider an abi-120 otic source of atmospheric CH_4 from the oxidation of acetaldehyde. In the next section 121 we describe our developed 1-D model of Mars photochemistry. In section 3 we report re-122 sults from our numerical experiments. We conclude the paper in section 4 in which we 123 discuss the implications of our results for broadly understanding atmospheric chemistry 124 on Mars but in particular the implications for detecting the presence of CH_4 and C_2H_6 125 on Mars using their oxidation products. 126

127 2 1-D Photochemical Model

We use the 1-D photochemistry submodule from the parent 3-D LMD-UK Mars General Circulation Model as the basis for a standalone 1-D model that includes an improved treatment of atmospheric organic photochemistry.

We use this standalone 1-D model to describe time-dependent vertical distributions 131 of trace gases from the surface to an altitude of approximately 70 km, described by 25 132 vertical layers with a resolution of under 0.5km below 2 km increasing to a resolution 133 of 10 km above an altitude of 20 km where 3-D macroscopic processes begin to domi-134 nate. We divide a Mars sol into 48 time steps ($\Delta t = 1800$ s), allowing us to describe di-135 urnal variations of trace gases by calculating time-dependent changes in solar zenith an-136 gle, taking into consideration changes in solar longitude and axial tilt. To decrease the 137 stiffness of the discretized equations used to compute the photochemical rates of change. 138 determined by a prescribed chemical mechanism described below, we use a chemistry sub-139 timestep of $\Delta t_c = 600$ s. 140

Vertical tracer transport between model layers is described by the classical diffusion equation (Mellor & Yamada, 1982). For details on the vertical diffusion and turbulent mixing routines we refer the reader to Forget et al. (1999). We use a radiative transfer scheme (Madeleine et al., 2011) that uses opacity values from the Mars Climate Database v5.3. We describe the condensation and sublimation of carbon dioxide, (Forget et al., 1998), water ice (Navarro et al., 2014), and hydrogen peroxide (H₂O₂); and an implicit chemistry solver computes production and loss rates from photochemical reactions.

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2.1 Organic Photochemistry

The 1-D submodel that resides in the LMD-UK MGCM describes the atmospheric chemistry and transport of 15 trace gases: carbon dioxide (CO₂), carbon monoxide (CO), atomic oxygen (O), singlet oxygen (O(¹D)), molecular oxygen (O₂), ozone (O₃), hydrogen atom (H), hydroxy radical (OH), hydroperoxyl radical (HO₂), molecular hydrogen (H₂), hydrogen peroxide (H₂O₂), nitrogen (N₂), argon (Ar), and H₂O as ice and vapour. The photochemistry scheme for these compounds consists of 32 chemical reactions (B1), and 10 photolysis reactions (B2).

¹⁵⁶ We build on the chemical mechanism by including 41 new organic compounds, guided ¹⁵⁷ by previous studies (Wong et al., 2003; Summers et al., 2002) and also the theoretical ¹⁵⁸ measurement capabilities of the NOMAD instrument (Robert et al., 2016), to improve ¹⁵⁹ understanding of Mars' atmospheric chemistry. We include CH_4 , C_2H_6 and its photo-¹⁶⁰ chemical products. The extended chemical mechanism represents an additional 106 chem-¹⁶¹ ical reactions (B1) and 29 photolysis reactions (B6). A complete list of trace gas species within the 1-D model is provided in Table 1. We present the first analysis of C_2H_6 oxidation products in the Martian atmosphere.

We take the organic chemistry rate coefficients from the CAABA/MECCA v4.0 164 atmospheric box model (R. Sander et al., 2019), which is used to model organic chem-165 istry within Earth's atmosphere. We have modified the mechanism to include HCO and 166 C_2H_5 radicals. The CAABA/MECCA v4.0 model neglects these radicals as products, 167 and instead includes the products of the radicals with molecular oxygen, O_2 . This ap-168 proximation is sufficient for Earth, where O_2 is present at 21% mass fraction, but on Mars 169 it is present only at a mass fraction of 10^{-3} . Including these radicals allows us to im-170 prove the description of organic chemistry. All three-body reaction rate coefficients in 171 the submodule are multiplied by a factor of 2.5, following Nair et al. (1994), to account 172 for the increase in efficiency that CO₂ displays when used as a bath gas in comparison 173 to N_2 or dry air (Kaufman & Kelso, 1967), commonly used in laboratories for the cal-174 culation of these coefficients. 175

To improve the accuracy of the original chemistry routine and to reduce the com-176 putational expediency of our chemistry calculation we use a pre-calculated look-up ta-177 ble to interpolate photolytic frequencies. We calculated these photolysis loss rates us-178 ing the Tropospheric Ultraviolet and Visible (TUV) Radiation Model (Madronich et al., 179 2002) that has been adapted for use on Mars (Lefèvre et al., 2004), and using routines 180 to interpolate as function of atmospheric temperature, solar zenith angle, O_3 column den-181 sity, the total atmospheric column density, the Sun-Mars distance, and the dust opac-182 ity. The photolytic reaction j_{HOCH_2OOH} of B6 requires the consideration of the abun-183 dance of O_2 , as the photolytic product of HOCH₂OOH is the highly reactive HOCH₂O 184 radical. HOCH₂O proceeds to react with molecular oxygen to form HCOOH and OH. 185 To limit the number of compounds that the steady-state approximation has to be ap-186 plied to, the 1-D model multiplies the photolytic frequency extracted from the TUV look-187 up table by a temperature independent factor of 3.50×10^{-14} (Veyret et al., 1982) and 188 the number density of O_2 at the respective layer. 189

To improve the accuracy of the original chemistry routine and to reduce the stiff-190 ness of the chemistry calculations, we decreased the chemical timestep to 600 seconds. 191 This has the additional benefit of allowing the Semi-Implicit Backward Euler Method 192 (SIBEM) to be used for a larger number of species across timestep Δt_c while conserv-193 ing mass of the studied tracers. For species with photochemical lifetimes shorter than 100 seconds we consider a family of species, e.g. odd-hydrogen (HO_x) and odd-oxygen 195 (O_x) families, which have a collective lifetime longer than the timestep. We handle these 196 compounds, H, OH, HO_2 and $O(^{1}D)$, $O(^{3}P)$, O_3 respectively via the assumption of pho-197 tochemical equilibrium (Rodrigo et al., 1990). The routine calculates dimensionless par-198 tition functions of the loss rates of H/HO_2 , OH/HO_2 , and $O(^{3}P)/O_3$ (s⁻¹/s⁻¹), and sums 199 the abundances of each family, HO_x and O_x , which possess atmospheric lifetimes greater 200 than that of the chemistry timestep, allowing them to be computed via the SIBEM equa-201 tion. The partition functions are then applied to compute each individual compounds 202 respective abundance. 203

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2.2 Time-dependent meteorological boundary conditions

To drive the 1-D photochemistry model, we use time-dependent lateral atmospheric boundary conditions of temperature, wind, water vapour volume mixing ratios, and surface pressure from the Mars Climate Database v5.3 (MCD) (Millour et al., 2017). We interpolate the 3-D meteorological fields from the MCD dataset, taking into account latitude, solar longitude, and local time.

All interpolated values from the MCD dataset are longitudinal means, calculated independently by ourselves, acknowledging that there are only small longitudinal variations of meteorological parameters that are due primarily to topographical features. We

Formula	Name
Ino	rganic Tracers
CO_2	Carbon Dioxide
	Carbon Monoxide
$O(^{1}D)$	Atomic Oxygen (excited singlet)
$O = O(^{3}P)$	Atomic Oxygen (ground state)
O = O(1)	Molecular Ovygen
O_2	Orana
O_3	Ozone
н	Atomic Hydrogen
OH	Hydroxyl
HO_2	Hydroperoxyl
H_2O_2	Hydrogen Peroxide
H_2	Molecular Hydrogen
H_2O (vapour and ice)	Water Vapour and Ice
N_2	Nitrogen
Ar	Argon
Organic Trace	ers (Methane Oxidation)
CH ₄	Methane
CH_3	Methyl Radical
CH ₂ O ₂	Methyl Peroxy-radical
CH-OOH	Methyl Hydroperoxide
CH_OH	Methanol
CH_O	Mathovido
	Formaldabuda
нспо	Formaidenyde
HCOOH	Formic Acid
$HOCH_2O_2$	Hydromethyl Peroxy
HOCH ₂ OH	Methanediol
$HOCH_2OOH$ HCO	Hydromethyl Hydroperoxide Formyl Radical
Organic Trac	ers (Ethane Oxidation)
CaHe	Ethane
C_2H_0 C_2H_2	Ethyl Badical
$C_2 H_2 O_2$	Ethyl Radical
$C_{2115}O_{2}$	Ethel Deveside
C_2H_5OOH	Ethyl Peroxide
C_2H_5OH	Etnanol
$HOCH_2CH_2O_2$	-
HOCH ₂ CH ₂ O	-
Ethgly ($(CH_2OH)_2$)	Ethylene Glycol
Hyetho2h ($C_2H_6O_3$)	-
CH_3CHO	Acetaldehyde
CH_2CHOH	Ethenol
CH_3CHOHO_2	Hydroxy Ethyl Peroxy Radical
CH ₃ COOH	Acetic Acid
CH ₃ CHOHOOH	-
$CH_3C(O)$	Acetyl Radical
$CH_3C(O)OO$	
CH ₂ C(O)OOH	Peracetic Acid
HCOCHAOA	
Ω_{1000}	-
HCOCO	Giyoxai
НООСН-СНО	- Hydroperovy Acataldabyda
	Chrooladabrda
HOCHCHO	nyaroxyi-vinoxy Kadical
$HOCH_2CO$	-
$HOCH_2CO_3$	-
$HOCH_2CO_2H$	Glycolic Acid
$HCOCO_2H$	-
$HCOCO_3H$	-
$HCOCO_3$	-
HOCH ₂ CO ₃ H	-
-	

Table 1.	Trace gas species handled by the 1-D photochemistry submodule.
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take advantage of this so that the horizonal footprint of our model is representative of 213 a zonal band of 3.75° in latitude, which is the latitudinal resolution of the MCD dataset. 214 Zonal and meridional transport is not accounted for by the 1-D model. We use an in-215 terpolation routine for trace gases that have atmospheric chemistry lifetimes greater than 216 the e-folding residence times associated with meridional advection of trace gases out of 217 the zonal band, which is approximately 0.5-2 sols. We use this approach to drive the model 218 with vertical profiles of CO₂, CO, O₂, H₂, and water vapour, ensuring the photochem-219 ical environment is consistent with the meteorological fields from the MCD, allowing the 220 1-D model to be accurately representative of the temporally and spatially variable ox-221 idising environment. Seasonal water vapour profiles from MCD are especially important 222 for the 1-D photochemical calculations as the photolysis of Martian H_2O is the source 223 of the highly reactive odd-hydrogen species, $HO_x = H + OH + HO_2$, which help drive 224 the oxidation of organic species and O_3 chemistry (Lefèvre et al., 2004). 225

The overarching purpose of using these boundary conditions is that we can describe 226 detailed 1-D atmospheric chemistry, including diurnal and seasonal changes associated 227 with Mars' atmosphere, without the computational overhead of solving the 3-D dynam-228 ical equations. In particular, the boundary conditions help to maintain realistic values 229 and variations of wind profiles that underpin vertical diffusion calculations that corre-230 spond to calculating vertical transport. For all of our calculations, we use a prescribed 231 dust scenario produced from the assimilation of observations of the dust optical depth 232 made by the Mars Global Surveyor's Thermal Emission Spectrometer (Montabone et al.. 233 2015) during Mars Year (MY) 24. This scenario is regarded as a 'best guess' of the mean 234 annual dust variability experienced on Mars without the presence of global or significant 235 regional dust storms. The 1-D photochemical model is capable of operating in dust-storm 236 scenarios using data from the MCD v5.3, but these calculations are beyond the scope 237 of the current study. 238

We limit our calculations to latitudes less than 30° , where most recent observations 230 of CH_4 on Mars have been reported (Mumma et al., 2009; Webster et al., 2018, 2015) 240 At latitudes higher than 40° in both hemispheres, the MCD boundary conditions also 241 allow us to describe the large-scale seasonal changes in atmospheric temperature that 242 result from condensation, deposition and sublimation of CO_2 , which produce significant 243 changes in surface pressure. However, at these latitudes meridional wind profiles above 244 the planetary boundary layer can become large enough to lower the tracer e-folding timescales 245 to values too small for the 1-D model to neglect while still producing reliable model re-246 sults. At latitudes less than 30° , the 1-D model in this work can be used to produce time-247 dependent tracer profiles for periods limited to 2 sols. 248

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2.3 Definition of Numerical Experiments

We use the 1-D model to determine vertical profiles of organic compounds that evolve from a hypothetically fixed and vertically uniform 50 pptv profile of CH₄. We have chosen this value because it is consistent with the upper limit of Martian CH₄ determined by data collected from the ACS/NOMAD instruments aboard the TGO (Korablev et al., 2019).

For this calculation, we initialise the model 10 sols prior to the point where solar 255 longitude $L_S = 0^{\circ}$ with initial meteorological conditions and tracer profiles of CO₂, CO, 256 O_2 , water vapour, and H_2 from the previously detailed MCD v5.3 look-up table, and 10 257 ppbv of CH_4 distributed evenly across all 25 atmospheric layers ranging from the sur-258 face to approximately 70 km. We then run the 1-D over one Mars year, 668 sols, follow-259 ing a 10 sol spin-up period, taking into account diurnal and seasonal (orbital) variations 260 in solar zenith angle and corresponding changes in solar flux and photolytic frequencies. 261 We report calculations at latitudes of 30°N, 2.5°N, and 30°S to investigate possible spa-262 tial variations in organic product profiles. 263

Following this investigation into the annual variations of the products produced by 264 the steady and homogeneous CH_4 background, we use the 1-D model to investigate time-265 dependent photochemical processes that result from oxidation of CH_4 and C_2H_6 . For 266 these experiments, we initialise the 1-D model at the required latitude and solar longitude at 00:00 local time (LT) with 0 pptv CH_4 and other non-methane organic compounds. 268 We use a five-day spin-up period at a constant solar longitude when we use trace gas pro-269 files of CO₂, CO, O₂, H₂, and water vapour from the MCD v5.3 (section 2.2) and diurnally-270 varying atmospheric parameters. This spin-up enables the HO_x and O_x chemistry to par-271 tition to the solar-longitude environment. After five sols, we add a vertically-uniform 50 pptv 272 profile of CH_4 at 00:00 LT. We then let the model run freely for one further sol, and present 273 the photochemical products at a local time of 18:00 LT when solar occultation measure-274 ments are typically collected. We adopt a similar approach to examine the photochem-275 istry of C_2H_6 . 276

277 **3 Results**

We use the 1-D model described in the previous section to understand the seasonal chemical composition of the Martian atmosphere as a function of latitude that corresponds to a fixed, uniform vertical distribution of atmospheric CH_4 . We present a similar set of calculations that correspond to a uniform vertical distribution of atmospheric C_2H_6 .

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3.1 Methane Oxidation in the Atmosphere of Mars

Figure 1 describes the initial photochemical oxidation steps of atmospheric CH₄ 283 on Mars. The dominant atmospheric losses of CH_4 are oxidation by the hydroxyl rad-284 ical (OH) and the excited singlet oxygen $(O(^{1}D))$, and photolysis. The loss rates for at-285 mospheric CH_4 vary as a function of solar longitude. There are a number of high-yield 286 oxidation products that are produced rapidly, potentially allowing us to colocate elevated 287 values with CH₄ emissions, and that are observable from orbiting instruments. In this 288 paper we will restrict our analysis to the production of formaldehyde (HCHO) and formic 289 acid (HCOOH). 290

Figure 2 shows an illustrative vertical distribution of CH_4 loss factors (s⁻¹) at the solar longitudes of 71° and 271°, times at which Mars' orbit is furthest from and closest to the Sun, respectively. Loss factors, units of s⁻¹, are distinguished from loss rates, units of molec cm⁻³s⁻¹, as loss factors provide a better insight into the reactivity of the surrounding environment. These values after being multiplied by CH_4 number densities equate to the rate of photochemical loss of CH_4 (molec cm⁻³s⁻¹), i.e. the loss rate.

From the Martian surface to the top of the Martian hygropause, approximately 10 km 297 at L_S 71° and 45 km at L_S 251°, the dominant loss process for CH₄ is from oxidation by 298 OH. Consequently, at these altitudes the rate of OH production, driven by the photol-299 vsis of water vapour, are larger than outside this altitude range. Above these altitudes, 300 the abundance of $O(^{1}D)$ increases, reflecting the drop in its loss from reaction with wa-301 ter vapour. Between the top of the hygropause and roughly 60 km, $O(^{1}D)$ becomes the 302 dominant loss of atmospheric CH_4 . There are three oxidation channels associated with 303 this reaction (B4), the most efficient producing CH_3 and OH. Photolysis of CH_4 becomes 304 significant only at altitudes higher than 60 km. The decreasing abundance of $O(^{1}D)$ atoms 305 in the upper atmosphere results in a small vertical region, 50-60 km, where CH₄ loss rates 306 decline before photolysis becomes important at higher altitudes. Below 60 km, the ef-307 fect of UV radiation on CH₄ is negligible, and photochemical contributions made by methyl 308 radical isotopologues can be disregarded. This highlights that the primary atmospheric 309 sinks of CH_4 change seasonally, with $O(^1D)$ dominating in the aphelion seasons, and OH310 dominating in the perihelion. The stronger reaction rates of $O(^{1}D)$ with CH₄ can thus 311 be expected to produce greater abundances of potentially observable organic species within 312 the aphelion seasons of Mars. 313



Figure 1. Primary stages of the CH₄ photochemistry that we use in our 1-D photochemistry model, taken from the CAABA/MECCA v4.0 chemical mechanism.

The local atmospheric lifetime of CH₄, incorporating all chemical loss terms (Fig-314 ure 2), varies as a function of latitude and solar longitude. Differences between latitudes 315 are determined by the solar radiation being received, which is a function of solar longi-316 tude and Mars' obliquity. Local atmospheric lifetimes range from 25 to 1700 years (Ap-317 pendix A1). These values, with a significant and localized surface loss process, would gen-318 erate a large, slowly varying background value for CH_4 that would be difficult to attribute 319 to individual surface sources. Local atmospheric lifetimes reach a minimum of 25–200 320 years between the top of the hygropause and approximately 50 km due to the larger abun-321 dance of the $O(^{1}D)$ atom. Below the hygropause where OH is the dominant sink, local 322 atmospheric lifetimes vary between 200 and 425 years. The longest local lifetimes of 1000-323 1700 years lie between 50 and 60 km during winter ($L_S = 270-360^\circ$), as described above, 324 where the OH and $O(^{1}D)$ loss processes decline and before photolysis dominates above 325 60 km. 326

These local atmospheric photochemical lifetimes are significantly longer than the 327 corresponding atmospheric transport timescales across all altitudes and solar longitudes. 328 We study the variance of these local photochemical lifetimes with solar longitude, alti-329 tude, and Mars latitude to understand where are the most photochemically active re-330 gions for CH_4 (and below for C_2H_6) and consequently where we expect the largest pro-331 duction rates for their oxidation products. Calculating the vertically integrated photo-332 chemical lifetime of CH_4 with the 1-D model (Appendix A1) yields timescales that cor-333 respond well to those calculated in previous studies (Lefèvre & Forget, 2009; Krasnopol-334 sky et al., 2004; Summers et al., 2002), with the 1-D model producing values ranging be-335 tween 250-550 terrestrial years across the latitude ranges studied here of 30° south to 336 30° north. 337



Figure 2. Photochemical loss factors (s^{-1}) CH₄ in our 1-D photochemistry model at latitude 2.5°N, local time 12:00, and solar longitudes 71° and 251° (Mars' aphelion and perihelion, respectively) as a function of altitude.

Figure 3 shows vertical profiles of the volume mixing ratios of organic compounds, 338 radicals, peroxy-radicals, and long-lived species from left to right, that result from the 339 oxidation of a fixed, uniformly distribution 50 pptv of atmospheric CH_4 . For this cal-340 culation we initialise the 1-D model with 0 pptv of CH_4 across all vertical layers at L_S 341 = 71° and $L_S = 251^\circ$, 00:00 LT, at a latitude of 2.5°, the latitude at which a CH₄ plume 342 has been previously observed (Mumma et al., 2009). We spin-up for five sols using de-343 tailed MCD v5.3 tracer profiles (section 2). We then insert a fixed, uniform profile of 50 pptv 344 of CH_4 into the model and run forward for one sol. We sample the model at 18:00 LT 345 on sol 6, allowing sufficient time (18 hours) for products to be produced but a short enough 346 time to ensure these products are not advected out of the column. This allows us to study 347 the resulting CH_4 oxidation product concentrations. We show values for CH_4 , HCHO, 348 HCOOH, methanol, methyl hydroperoxide (CH₃OOH), hydromethyl peroxy (HOCH₂O₂), 349 and hydromethyl hydroperoxide (HOCH $_2$ OOH). The two products with the highest pho-350 tochemical yields are HCHO and HCOOH. We find that HCHO has column averaged 351 mixing ratios of 5.43×10^{-16} and 7.41×10^{-17} molecule/molecule at $L_S = 71^{\circ}$ and 251° , 352 respectively. HCOOH has a column averaged mixing ratio of 2.31×10^{-17} and 2.08×10^{-17} 353 molecule/molecule at $L_S = 71^{\circ}$ and 251° , respectively. We describe below the respon-354 sible production and loss rates associated with these two compounds. 355

Production rates of methanol are small in our 1-D model, which is driven by a re-356 alistic 50 pptv of CH_4 . Previous studies that have used a much larger 100 ppmv profile 357 of CH_4 (e.g. (Wong et al., 2003)) have still struggled to produce Martian methanol above 358 pptv values. CH_3OH has prominent features at IR wavelengths, making it a valuable ob-359 served species to help constrain our understanding of organic chemistry. Our 1-D model 360 calculates CH₃OH column average mixing ratios of 2.09×10^{-19} and 1.01×10^{-18} molecule/molecule 361 at $L_S = 71^{\circ}$ and 251° , respectively. These small quantities are due to the two main pro-362 duction terms for CH_3OH (Table B4) involving CH_3O_2 and CH_3 radicals that are not 363 produced in large quantities by 50 pptv of CH_4 . Consequently, we will only discuss CH_3OH 364 in context of HCHO and HCOOH. 365

366

3.2 Production of Formaldehyde from CH₄ Oxidation

HCHO is a high-yield oxidation product of CH₄ on Mars that is observable by the 367 NOMAD and ACS spectrometers aboard the Trace Gas Orbiter. Figure 4 shows verti-368 cal distributions of HCHO volume mixing ratios, corresponding to a fixed vertical pro-369 file of 50 pptv CH_4 , at 18:00 LT over all solar longitudes to determine when we might 370 expect HCHO to be observable during one Martian year. HCHO production peaks dur-371 ing spring months when there is sufficient production of $O(^{1}D)$ in the middle atmosphere 372 to oxidize CH_4 but not water vapour in the lower atmosphere. We find only small vari-373 ations in the HCHO produced across the three latitudes, where HCHO consistently re-374 mains below 10^{-3} pptv. This lies well below the expected detection limit of 30-40 pptv 375 for the TGO NOMAD instrument (Robert et al., 2016) and of 0.17–1.70 ppbv for the 376 TGO ACS instrument (Korablev et al., 2017). 377

Figure 5 shows individual and net production and loss rates of HCHO as a func-378 tion of altitude at 06:30 LT, $L_S = 71^{\circ}$, and latitude 2.5°N. We find net production peaks 379 at 06:30 LT as the Sun begins to rise above the horizon. Figure 5a shows two distinct 380 regions where HCHO production peaks. Below the hygropause, at roughly 15 km at this 381 L_S , reaction between water vapour and excited atomic oxygen result in HCHO produc-382 tion dominated by the reaction of CH_3O_2 and HO_2 . Above the hygropause at 15 km, 383 the HCHO production is from atomic oxygen reacting with methyl and methoxy rad-384 icals. Figure 5b show the HCHO loss rates. We find that HCHO is lost rapidly by pho-385 tolysis through the atmospheric column. Below the hygropause, HCHO is lost by reac-386 tion with HO_2 which produced the $HOCH_2O_2$ peroxy radical. Above the hygropause, 387 the dominant HCHO sink is reaction with atomic oxygen. At solar zenith angles between 388 60 and 85°, abundances of $O(^{3}P)$, CH₃, and CH₃O radicals are in large enough at the 389





Figure 3. Volume mixing ratio profiles of major photochemical products of 50 pptv of CH_4 after one sol. These include formaldehyde (HCHO), formic acid (HCOOH), methanol (CH_3OH), methyl hydroperoxide (CH_3OOH), hydromethyl peroxy ($HOCH_2O_2$), and hydromethyl hydroperoxide ($HOCH_2OOH$).

HCHO Annual Vertical Distributions



Figure 4. Vertical profiles of HCHO (pptv) from the photochemistry of 50 pptv CH_4 within a zonal band centered on latitudes $30^{\circ}N$, $2.5^{\circ}N$, and $30^{\circ}S$, across all solar longitudes, as calculated by our 1-D photochemical model.

top of the hygropause to overcome the loss of HCHO from photolysis. At lower solar zenith
 angles, the rate of formaledhyde photolysis is too great to allow significant net production.

The resulting atmospheric lifetime of HCHO for all Martian seasons is 2–6 hours 393 at latitudes less than 30° (Appendix A2), consistent with previously published results 394 (Wong et al., 2003). As a result, a detection of HCHO below 70 km in the Martian at-395 mosphere will require a strong active release of CH_4 in the local vicinity. Our calcula-396 tions suggest that HCHO will be most likely detected at mid-altitudes (15-30 km) across 397 the tropics during Mars northern spring and summer months. This is due to the lower 398 abundance of water vapor and the increased levels of odd-oxygen species available for 399 reactions with organic radicals, and also coincides with the altitude regions where the 400 TGO instruments are expected to display the greatest level of sensitivity (Korablev et 401 al., 2017). 402

Using 1-D steady-state model driven by a profile of 100 ppmv CH₄, (Wong et al., 403 2003) report an increase in HCHO above 50 km. Our 1-D calculations are time-dependent, 404 driven by a more realistic CH_4 value (published since (Wong et al., 2003)), and by in-405 terpolated atmospheric parameters that include optical opacity and long-lived inorganic 406 tracers from a 3-D dataset. As such, we believe our approach provides a more compre-407 hensive and realistic modelling environment to describe atmospheric photochemistry on 408 Mars. The photolysis loss rates for HCHO in our model at latitude 2.5° are compara-409 ble to those used by (Wong et al., 2003). Differences between our calculations and those 410 reported by (Wong et al., 2003) are mainly due to smaller quantities of radicals produced 411 by a much lower assumed value of atmospheric CH_4 , and our consideration of longitu-412 dinal mean variations of atmospheric parameters instead of using global mean param-413 eters. 414



Figure 5. Photochemical production and loss rates for HCHO (molec cm⁻³s⁻¹), associated with CH₄ photochemistry, as a function of altitude. Calculations are for $L_S = 71^{\circ}$, 06:30 LT, and latitude 2.5°N.



Figure 6. As Figure 5 but for formic acid (HCOOH).

3.3 Production of Formic Acid from CH₄ Oxidation

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The oxidation of HCHO via HO₂ radicals leads to pathways that produce HCOOH 416 (Figure 1). HCHO reacts with HO_2 to produce the $HOCH_2O_2$ peroxy radical, which can 417 either decay into its original reactants, or react with HO₂ to produce HCOOH directly 418 or to produce hydroxymethyl hydroperoxide that subsequently reacts with OH to pro-419 duce formic acid or HOCH₂O₂, with a branching ratio, $k_{HOCH_2O_2}/k_{HCOOH}$, of 0.233 at 420 298 K. HOCH₂OOH can also photolyse under UV radiation to produce HOCH₂O and 421 OH. The HOCH₂O radical proceeds to react with molecular oxygen to produce formic 422 acid and HO_2 . The only sink of HCOOH in the Martian atmosphere is via oxidation by 423 OH. This reaction is slow, and limits loss of HCOOH to regions below the point of the 424 hygropause. In regions where OH concentrations are at a maximum, typically during L_S 425 $= 150-340^{\circ}$ at the top of the water vapour saturation point, HCOOH has a photochem-426 ical lifetime that range between 1 and 10 sols. From the surface to roughly 8 km, val-427 ues range between 70 sols and 220 sols throughout the year in the northern hemisphere, 428 but values in the south increase to magnitudes of 10^3 sols during the northern summer 429 $(L_S = 90-180^\circ \text{ with the lower abundances of atmospheric } H_2O.$ 430

Figure 6 shows the net and individual production and loss rates for HCOOH for 431 $L_S = 71^{\circ}$, latitude 2.5°N, and LT = 18:00 due to a fixed, uniformly distribution of 50 pptv 432 CH_4 . The largest production rate of HCOOH is from $HOCH_2O_2$ reacting with HO_2 and 433 from the photolysis of HOCH₂OOH. The loss of HCOOH from OH oxidation is slow com-434 pared to the production rates. Our calculations therefore suggest that a detection of HCOOH 435 would be related to the photochemical loss of HCHO. The resulting atmospheric lifetime 436 of HCOOH is temporally and spatially variant, with lows of 2–5 sols at the tip of the hy-437 gropause, increasing to 75–100 sols closer to the surface where the abundances of OH 438 fall. 439

3.4 Ethane Oxidation

Here we consider the impact of C_2H_6 on Mars' photochemistry. The impetus for these calculations is that on Earth, emissions of CH_4 are accompanied by emissions of higher-chain hydrocarbon such as C_2H_6 (Horita & Berndt, 1999; Guenther et al., 2000). C_2H_6 is also listed as an observable compound through the NOMAD-SO and ACS-MIR instrument, with detection limits between 0.02 and 0.03 ppbv (Vandaele et al., 2018) and 0.06–6 ppbv (Korablev et al., 2017). Current knowledge puts an upper limit of 0.20 ppbv on C_2H_6 (Krasnopolsky, 2012; Villanueva et al., 2013).

Figure 7 shows that the photochemistry for C_2H_6 is more complicated than for CH_4 (B4), but follows the same general routes. It is oxidized by OH and O(¹D) that initiates a series of chemical reactions that result in high yield products of HCHO and HCOOH among other compounds. One of the initial C_2H_6 oxidation product is the C_2H_5 radical, which is not described explicitly by the CAABA mechanism. We have used independent sources for reaction rates that involve the C_2H_5 radical (B5).

Figure 8 shows the photochemical loss factors for C_2H_6 in the Martian atmosphere 454 at noon, L_S 71° and 251°, and at latitude 2.5°N. Our photolysis calculations, based on 455 values from the TUV model (Madronich et al., 2002) and adjusted for the Sun-Mars dis-456 tance, suggest this loss process is insignificant below 70 km. Similar to CH_4 , below the 457 Martian hygropause OH is the dominant loss process for C_2H_6 , and above the hygropause 458 $O(^{3}P)$ is the dominant loss process for $C_{2}H_{6}$, with the $C_{2}H_{5}O_{2}$ peroxy radical being a 459 common oxidation product that results in a cascade of photochemical reactions, as de-460 scribed in Figure 7. The resulting photochemical lifetime of C_2H_6 is typically between 461 1 and 3.5 years below altitudes of 5 km and much shorter (50–450 sols) above the hy-462 gropause. (Appendix A). 463

Figure 9 shows the vertical profiles of organic compounds produced by the oxida-464 tion of 50 pptv of C_2H_6 after one sol at L_S 71° and 251°, latitude 2.5° sampled at 18:00 LT, 465 to allow comparisons against the methane investigation of Figure 3. The introduction 466 of longer chain peroxy-radicals via the $C_2H_5O_2$ radical increases the richness of photo-467 chemical products that are produced from CH₄ oxidation. In particular, the oxidation 468 of C_2H_6 results in CH_3CHO column averaged mixing ratios of 7.24×10^{-16} molecule/molecule 469 at aphelion conditions, elevating to 3.18×10^{-15} molecule/molecule at perihelion condi-470 tions. UV photolysis of CH_3CHO is a source of CH_4 and carbon monoxide. We find that 471 UV photolysis of 50 pptv homogeneous column of C₂H₆ produces a CH₄ column aver-472 aged mixing ratio of 1.87×10^{-17} molecule/molecule at aphelion, and 3.97×10^{-16} molecule/molecule 473 at perihelion. The ratios of CH_4/C_2H_6 at aphelion and perihelion are 3.71×10^{-7} and 474 7.86×10^{-6} , respectively, and the ratio of CH₄/CH₃CHO at these two orbital points are 475 2.58×10^{-2} and 1.25×10^{-1} , respectively. 476

Formaldehyde is produced with a much higher yield for C_2H_6 oxidation than for 477 CH_4 oxidation, resulting in a column averaged mixing ratio of 3.16×10^{-15} and 5.74×10^{-14} 478 molecule/molecule at aphelion and perihelion, respectively. These yields are $\simeq 6$ times 479 and 777 times higher than those made by CH_4 at aphelion and at perihelion, respectively. 480 These higher yields of HCHO from C_2H_6 oxidation is due to a larger number of produc-481 tion pathways compared to the CH_4 oxidation mechanism. Production of HCOOH from 482 C_2H_6 photochemistry during perihelion, column mixing ratio 7.30×10^{-17} molecule, molecule, 483 is comparable with values from CH_4 oxidation, but is much smaller than CH_4 oxidation 484 during aphelion with a column mixing ratio of 1.34×10^{-18} molecule/molecule. Lower 485 production of HCOOH from C_2H_6 oxidation during aphelion is due to lower production 486 pathways for HOCH₂OOH and HOCH₂O₂, which drive subsequent production of HCOOH. 487



Figure 7. Primary stages of the C_2H_6 photochemistry that we use in out 1-D photochemistry submodule, taken from the CAABA/MECCA v4.0 box model.



Figure 8. Photochemical loss factors for C_2H_6 as a function of altitude in our 1-D photochemistry model with altitude. Calculations are for $L_S = 71^{\circ}$ and 251° , 12:00 LT, at latitude $2.5^{\circ}N$.



Lat. = 2.5° N, L_S = 71.3° , LT = 18:00 hrs

Figure 9. Volume mixing ratio profiles of oxidised organic products after one sol of introducing a uniform profile volume mixing ratio of 50 pptv of C_2H_6 .

3.5 Production of Formaldehyde and Formic Acid from C₂H₆ Oxida tion

Figure 10 shows the production and loss rates for HCHO and HCOOH from the oxidation of 50 pptv of C_2H_6 . The largest production rate of HCHO is below the hygropause from the reaction of CH_3O_2 peroxy radical with HO₂, comparable to values from CH_4 oxidation. However, above the hygropause at 20 km the three-body reaction $CH_3C(O)+O_2+M$ and the CH_3 radical reaction with atomic oxygen are the primary sources of HCHO. Combined, the HCHO production rate is an order of magnitude larger than the rate from CH_4 oxidation.

⁴⁹⁷ The higher reactivity of C_2H_6 produces a larger quantity of $HOCH_2O_2$ peroxy rad-⁴⁹⁸ icals and hydroperoxy radicals in the regions just above the hygropause compared to CH_4 ⁴⁹⁹ oxidation. With no additional loss processes, the increased net production rate results ⁵⁰⁰ in larger concentrations of HCOOH, with production falling off rapidly towards the sur-⁵⁰¹ face.

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3.6 Methane Production from the Oxidation of Acetaldehyde

Figure 11 shows production and loss rates of CH₄ associated with a 50 pptv homogeneous column of CH₃CHO at $L_S = 251^{\circ}$, latitude 2.5°, and at local noon to study the importance of UV photolysis of CH₃CHO. We calculate the photolysis loss rate using the TUV model (section 2) that penetrate efficiently to the surface. Net CH₄ production rates peak at 31.13 molec cm⁻³ s⁻¹, corresponding to an increase in CH₄ mixing ratio of 1.69×10^{-16} molecule/molecule s⁻¹, at $\simeq 1.30$ km above the Martian surface at this time of day. To our knowledge, this photolytic source of atmospheric CH₄ is the only proposed source that may be possible within the CO₂-dominated atmosphere of Mars.

511 4 Discussion and Concluding Remarks

We find that the oxidation of atmospheric CH_4 in the Martian atmosphere, at mag-512 nitudes similar to reported observations, produce formaldehyde and formic acid as pho-513 tochemical products but at volume mixing ratios too low for successful detection via re-514 mote sensing by the NOMAD and ACS spectrometers aboard the ExoMars Trace Gas 515 Orbiter. Our photochemical lifetimes of formaldehyde are consistent with previous stud-516 ies (e.g., Wong and Atreya (2004)), but we have also reported variations as a function 517 of altitude and solar longitude. Our use of the MCD v5.3 atmospheric parameters and 518 tracer profiles enabled us to deduce that the largest atmospheric lifetimes of HCHO at 519 latitudes less than 30° are typically around 4 hours during the northern spring and sum-520 mer above the point of H_2O vapour saturation. Our model expands upon the findings 521 from the steady state model by revealing the layered seasonal structure of HCHO that 522 can develop, whilst refining the modelled lifetimes and revealing the seasonal variabil-523 ity of the compound. 524

Our 1-D model refines the vertical structure and seasonal variability of the CH_4 525 within the equatorial regions of Mars, revealing that altitudes with low water vapour con-526 tent can provide $O(^{1}D)$ abundances large enough to suppress the lifetime of CH₄ to be-527 tween 50–100 years, shorter than previous estimates (Wong & Atreya, 2004; Summers 528 et al., 2002; Krasnopolsky et al., 2004). We reveal a region in the upper section of the 529 1-D model, corresponding to 50-70 km where the absence of OH, $O(^{1}D)$, and lower UV 530 photolysis increases CH_4 lifetimes to 400–800 years during the northern spring, and to 531 800–1300 years during the mid-northern summer to northern winter, significantly higher 532 than previous model estimations. Lifetimes close to the surface and below the hygropause 533 (0-30 km) are invariant with latitude during the northern spring, but display variations 534 between the north and southern hemisphere throughout the rest of the year, controlled 535 by the sublimation of the respective hemispheres polar caps water ice content. 536

HCHO



Figure 10. Photochemical production and loss rates (molec $\text{cm}^{-3}\text{s}^{-1}$) of HCHO and HCOOH



 CH_4

Figure 11. Photochemical production and loss rates for methane (molec cm⁻³s⁻¹), associated with the UV photolysis of a 50 pptv column of CH₃CHO, as a function of altitude. Calculations are for $L_S = 251^{\circ}$, 12:00 LT, and latitude 2.5°N.

We find that the photochemical lifetime of C_2H_6 is correlated to the atmospheric 537 water vapour content on Mars. Within the hygropause, lifetimes are found to be within 538 3-4 years, where OH is the dominant photochemical sink. At higher altitudes, these life-530 times are reduced to 100-400 Mars sols (0.15-0.6 years), due to the higher abundance 540 of atomic oxygen. The lifetimes of acetaldehyde reach values of approximately one sol 541 close to the Martian surface across all equatorial latitudes during the northern spring, 542 that lower to roughly 0.5 sols in the northern hemisphere summer to winter periods. Acetic 543 acid displays a similar seasonal trend, with lifetimes in the northern spring being between 544 3 and 4 sols below the hygropause, and lowering to between 0.2-1 sol with the eleva-545 tion of the water saturation point. Oxidation of C_2H_6 in the Martian atmosphere results 546 in a distinct profile of acetaldehyde, as well as greater yields of HCHO and HCOOH, com-547 pared to CH_4 oxidation. The 1-D model predicts atmospheric lifetimes of between 15 548 and 32 hours below altitudes of 25 km during $L_S = 0-135^\circ$, lowering to 4-12 hours out-549 side of this time frame across all equatorial latitudes, for CH_3CHO . We therefore pro-550 pose that any instrument detection of CH₃CHO can be attributed to a surface release 551 of C_2H_6 within the immediate local environment of the site of observation. 552

Our more comprehensive description of atmospheric chemistry, involving 135 or-553 ganic reactions, significantly expands on the schemes used by Wong and Atreya (2004) 554 and Summers et al. (2002). No formic acid was reported by the model of Wong and Atreya 555 (2004) for their 1-D steady state model with 100 ppmv of CH₄, whereas we report vol-556 ume mixing ratios of similar magnitude to HCHO below the hygropause with CH₄ abun-557 dances of 50 pptv, the current upper limit on Mars derived in Korablev et al. (2019). This 558 discrepancy can be explained by our more detailed description of peroxy radical chem-559 istry that is taken from the CAABA/MECCA v4.0 chemistry scheme. In our 1-D model 560 photochemical lifetimes of HCOOH are inversely proportional to the abundance of OH 561 available. At the top of the hygropause, lifetimes have magnitudes of 1 - 10 sols. Below, 562 the lifetimes vary substantially depending on the water vapour availability. Below 5 km, 563 photochemical lifetimes in the drier southern latitudes can reach values exceeding 10^3 564 sols, whereas in the north, values between 10 and 100 are commonly found. These long 565 photochemical lifetimes of HCOOH, in comparison to HCHO, makes it the most likely 566 photochemical product of CH_4 oxidation that could provide independent verification of 567 CH₄. Spectral features of HCOOH lie within the IR wavelengths measured by the ACS 568 aboard the TGO, and the long wave channel of the PFS covers the wavenumber range 569 of $250-1700 \text{ cm}^{-1}$ (Formisano et al., 2005) that includes two absorption features of the 570 HCOOH molecule (Gordon et al., 2017). 571

We find that the introduction of CH_4 at magnitudes similar to an empirically de-572 rived upper limit (<50 pptv) fails to produce significant perturbations to CO, O₃, or H₂O 573 vapour (not shown) that will observable by instruments aboard the TGO. CH_4 reactions 574 with $O(^{1}D)$ above the hygropause and below 50 km have the net effect of increasing OH 575 concentrations by magnitudes of 10^{-3} % after one sol of exposure, which results in cat-576 alyzing the conversion of CO to CO_2 via reaction e_1 of B1. The increase in OH arises 577 from the previously described reactions of $O({}^{1}D)$ atoms reacting with CH₄ in the drier 578 altitudes, most notably reaction b₇. CO experiences relative perturbations of $-10^{-6}\%$ 579 in the mid-altitudes, which will be lost within instrumental noise. This rise in OH, and 580 the loss of $O(^{1}D)$ to CH₄ interactions and $O(^{3}P)$ with organic radical interactions, re-581 sults in a drop in O_3 production in this region and increased O_3 loss. These perturba-582 tions are small, however, with drops of 10^{-3} % after one sol, an amount that is below in-583 strument signal-to-noise values. This highlights that source regions of CH_4 will not be 584 identifiable by perturbations made to inorganic trace gas species observable to the Ex-585 oMars Trace Gas Orbiter. 586

Finally, our model highlights the possible existence of an atmospheric source of CH_4 from the photolysis of CH_3CHO , an oxidation product of C_2H_6 . Photolysis of CH_3CHO in the Martian atmosphere is capable of producing trace amounts of CH_4 at all altitudes ⁵⁹⁰ above the surface. We find that 50 pptv of CH₃CHO is capable of producing CH₄ at a ⁵⁹¹ volume mixing ratio rate of 4.54×10^{-16} s⁻¹.

This opens up the possibility of further studying CH_3CHO as a possible source for CH₄ detection on Mars. Although no evidence exists for CH_3CHO on Mars, one hypothetical source could be due to a sub-surface acetylene hydratase (Rosner & Schink, 1995) enzyme that converts acetylene (C_2H_2) to CH_3CHO through reactions with liquid water.

Appendix A Martian Atmospheric Lifetimes of Methane, Formalde hyde, Formic Acid, and Ethane

A1 Methane

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Figure A1 shows the net atmospheric lifetime of CH_4 , incorporating all loss terms (Figure 2), as a function of latitude and solar longitude. Atmospheric lifetimes reach a minimum of 25–400 year between the top of the hygropause and approximately 50 km due to the larger abundance of the O(¹D) atom. Below the hygropause where OH is the dominant sink, atmospheric lifetimes vary between 400 and 800 years. The longest lifetimes of 800–1600 years lie between 50 and 60 km during winter ($L_S = 270-360^{\circ}$), as described above, where the OH and O(¹D) loss processes decline and before photolysis dominates above 60 km.

Variations in atmospheric lifetime are driven by the position of the Martian hygropause 608 and the water vapour content beneath, which is determined by 3-D model output from 609 the MCD (section 2). Water vapour columns reach their maximum during hemispheric 610 summer months when polar water ice sublimates with rising atmospheric temperatures. 611 SPICAM water vapour column measurements at $L_S = 50^{\circ}$ (Fedorova et al., 2006) show 612 only small variations at latitudes less than 30° , with values ranging from 2–10 pr μ m, 613 with saturation values under 25 km. This is consistent with our model loss processes that 614 determine the variation in atmospheric lifetime. Above 50 km, the stronger flux of so-615 lar radiation in the northern hemisphere due to the planets axial tilt results in a larger 616 abundance of $O(^{1}D)$ and a subsequent lower photochemical lifetime of CH_{4} than in the 617 southern hemisphere. As water vapour column abundances and saturation altitudes in-618 crease with L_S , the low latitude atmospheric lifetime of CH_4 increases below 50 km due 619 to H_2O reacting with $O(^1D)$ and decreases below roughly 25 km. The decrease in solar 620 flux during northern autumn and winter months ($L_S = 180^{\circ} - 360^{\circ}$) reduces the produc-621 tion rate of $O(^{1}D)$ relative to the southern hemisphere, which explains the variation in 622 lifetimes between the hemispheres. 623

624 A2 Formaldehyde

Figure A2 shows the resultant seasonal variability of HCHO lifetime at latitudes 30°N, 2.5°N, and 30°S. We find the longest lifetimes, between 4 and 5 hours, are found below 5 km in the southern hemisphere during the northern summer/southern winter, when this region contains low levels of water vapour.

A3 Formic Acid

629

Figure A3 shows the resultant seasonal variability of HCOOH lifetime at latitudes 30°N, 2.5°N, and 30°S. The lifetime of HCOOH is anti-correlated with water vapour, as expected. The longest lifetime (of magnitude's greater than 10⁴ sols) is during the northern spring at altitudes greater than 60 km where OH is lowest. As OH values increase with the supply of water vapour from northern polar ice sublimation, atmospheric lifetimes falls to 1–10 sols close to the hygropause and 10–200 sols at lower altitudes closer to the surface (below 5 km).



CH₄ Photochemical Lifetime

Figure A1. Local and vertically integrated photochemical lifetime of CH_4 within the atmosphere of Mars and its variations with altitude (km) and solar longitude at latitudes $30^{\circ}N$, 2.5 °N, and $30^{\circ}S$, respectively. All vertical segments are values from the 1-D photochemistry model at 12:00 LT.



Figure A2. Photochemical lifetime of HCHO within the atmosphere of Mars and its variations with altitude (km) and solar longitude at latitudes 30°N, 2.5 °N, and 30°S, respectively. All vertical segments are values from the 1-D photochemistry model at 12:00 LT.



Figure A3. Photochemical lifetime of HCOOH within the atmosphere of Mars and its variations with altitude (km) and solar longitude at latitudes 30°N, 2.5 °N, and 30°S, respectively. All vertical segments are values from the 1-D photochemistry model at 12:00 LT. Contour map saturated for values greater than 0.45 years.

With atmospheric lifetimes of this length, describing seasonal changes in HCOOH 637 profiles using a 1-D photochemistry model becomes problematic due to the photochem-638 ical lifetimes exceeding the venting timescales associated with our 3.75° thick zonal band 639 that our model represents. Without horizontal transport equations to describe the loss 640 of HCOOH to the zonal band edges, the resultant profiles after a one-year 1-D model 641 run will be subject to gross inaccuracies. As previously discussed in section 2, solving 642 the 1-D model equation for steady state conditions will not yield useful information due 643 to the observed temporal and localized nature of CH_4 emissions, invalidating the notion 644 of a steady-state environment. 645

A4 Ethane

646

Figure A4 shows that C_2H_6 has longer photochemical lifetimes below the points of H₂O saturation, where we find typical values that range from 3 to 5 years. In the middle atmosphere, the large abundance of O(³P) reduced the lifetime to 30–450 sols. Based on these calculations, we suggest that any detection of C_2H_6 made by the TGO instruments will due to an active release.



C₂H₆ Photochemical Lifetime

Figure A4. Local and vertically integrated photochemical lifetime of C_2H_6 within the atmosphere of Mars and its variations with altitude (km) and solar longitude at latitudes 30°N, 2.5 °N, and 30°S, respectively. All vertical segments are values from the 1-D photochemistry model at 12:00 LT.

Table B1. Inorganic reaction rate coefficients within the 1-D photochemistry submodule. Bimolecular rate coefficient units are cm³ molec⁻¹ s⁻¹. Values denoted by superscript *a* are threebody reactions with values taken with atmospheric number density complying to temperatures of T = 298 K and pressures of 660 Pa.

Key	Reaction	Formula	Rate at T = 298 K	Reference	
	Reactions with O				
a_1	$O + O_2 + M \rightarrow O_3 + M$	$2.075 \times 6.00 \text{E-} 34 (\text{T}/300)^{-2.4}$	2.23E-16 ^a	(S. Sander et al., 2003)	
a_2	$O + O + M \rightarrow O_2 + M$	$2.50 \times 9.46 \text{E} - 34 \exp(485/\text{T})$	2.10E-15 ^a	(Campbell & Gray, 1973)	
a_3	$O + O_3 \rightarrow O_2 + O_2$	8.00E-13exp(-2060/T)	7.96E-16	(S. Sander et al., 2003)	
		Reactions with $O(^1D)$			
b_1	$O(^{1}D) + CO_{2} \longrightarrow O + CO_{2}$	7.40E-11exp(120/T)	1.11E-10	(S. Sander et al., 2003)	
b_2	$O(^{1}D) + H_{2}O \longrightarrow OH + OH$	1.63E-10exp(60/T)	1.99E-10	(S. Sander et al., 2006)	
b_3	$O(^1D) + H_2 \longrightarrow OH + H$	1.20E-10	1.20E-10	(S. Sander et al., 2011)	
b_4	$O(^1D) + O_2 \longrightarrow O + O_2$	3.30E-11exp(55/T)	3.97E-11	(S. Sander et al., 2006)	
b_5	$O(^1D) + O_3 \longrightarrow O_2 + O_2$	1.20E-11	1.20E-11	(S. Sander et al., 2003)	
b_6	$O(^1D) + O_3 \longrightarrow O_2 + O + O$	1.20E-11	1.20E-11	(S. Sander et al., 2003)	
b_7	$O(^{1}D) + CH_{4} \longrightarrow CH_{3} + OH$	0.75×1.75E-10	1.31E-10	(S. Sander et al., 2003)	
b_8	$O(^{1}D) + CH_{4} \longrightarrow CH_{3}O + H$	0.20×1.75E-10	3.50E-11	(S. Sander et al., 2003)	
b_9	$O(^{1}D) + CH_{4} \longrightarrow HCHO + H_{2}$	$0.05 \times 1.75 \text{E-}10$	8.75E-12	(S. Sander et al., 2003)	
	F	Reactions with Hydrogen Compoun	ds		
c_1	$O + HO_2 \longrightarrow OH + O_2$	3.00E-11exp(200/T)	5.87E-11	(S. Sander et al., 2003)	
c_2	$O + OH \longrightarrow O_2 + H$	1.80E-11exp(180/T)	3.29E-11	(S. Sander et al., 2011)	
c_3	$H + O_3 \longrightarrow OH + O_2$	$1.40 \text{E} \cdot 10 \exp(-470/\text{T})$	2.89E-11	(S. Sander et al., 2003)	
c_4	$H + HO_2 \longrightarrow OH + OH$	7.20E-11	7.20E-11	(S. Sander et al., 2006)	
c_5	$H + HO_2 \longrightarrow H_2 + O_2$	6.90E-12	6.90E-12	(S. Sander et al., 2006)	
c_6	$H + HO_2 \longrightarrow H_2O + O$	1.60E-12	1.60E-12	(S. Sander et al., 2006)	
c_7	$OH + HO_2 \longrightarrow H_2O + O_2$	4.80E-11exp(250/T)	1.11E-10	(S. Sander et al., 2003)	
c_8	$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$	1.50E-12exp(19/T)	1.60E-12	(Christensen et al., 2002)	
C_9	$OH + H_2O_2 \longrightarrow H_2O + HO_2$	1.80E-12	1.80E-12	(S. Sander et al., 2006)	
c_{10}	$OH + H_2 \longrightarrow H_2O + H$	2.80E-12exp(-1800/T)	6.67E-15	(S. Sander et al., 2006)	
c_{11}	$H + O_2 + M \longrightarrow HO_2 + M$	k_3rd(2.5×4.4E-32, -1.3, 7.5E-11, 0.2)	1.88 E-14 a	(S. Sander et al., 2011)	
c_{12}	$O + H_2O_2 \longrightarrow OH + HO_2$	1.40E-12exp(-2000/T)	1.70E-15	(S. Sander et al., 2003)	
C13	$OH + OH \longrightarrow H_2O + O$	1.80E-12	1.80E-12	(S. Sander et al., 2006)	
C14	$OH + O_3 \longrightarrow HO_2 + O_2$	$1.50 \text{E} \cdot 12 \exp(-880/\text{T})$	7.83E-14	(S. Sander et al., 2003)	
C15	$HO_2 + O_3 \longrightarrow OH + O_2 + O_2$	$1.00\text{E}\text{-}14\exp(-490/\text{T})$	1.93E-15	(S. Sander et al., 2003)	
c_{16}	$HO_2 + HO_2 + M \longrightarrow H_2O_2 + O_2 + M$	$2.50 \times 2.10 \text{E} - 33 \exp(920/\text{T})$	2.01E-14 ^a	(S. Sander et al., 2011)	
c_{17}	$OH + OH + M \longrightarrow H_2O_2 + M$	$k_3rd(2.5 \times 6.9E-31, -1, 2.60E-11, 0)$	2.70 E-13 a	(S. Sander et al., 2003)	
c_{18}	$H + H + M \longrightarrow H_2 + M$	$2.5 \times 1.80 \text{E-}30/\text{T}$	2.64 E-14 a	(Baulch et al., 2005)	
		Carbon Compounds			
e_1	$OH + CO \longrightarrow CO_2 + H$	Details in Joshi and Wang (2006)	1.47E-13	(Joshi & Wang, 2006)	
e_2	$O + CO + M \longrightarrow CO_2 + M$	$2.5 \times 6.50 \text{E-} 33 \exp(-2184/\text{T})$	$1.87E-18^{\ a}$	(Tsang & Hampson, 1986)	

⁶⁵² Appendix B Reaction Rate Coefficients

Table B2. Photolytic reactions of inorganic compounds used within the 1-D photochemistry submodule. Values (s⁻¹) are interpolated from an offline look-up table constructed by a modified TUV (Madronich et al., 2002) model with respect to CO₂ and O₃ column abundances overheard, temperature, optical opacity and solar zenith angle. Values displayed are for a solar zenith angle of 0°, $L_S = 251^{\circ}$ (perihelion).

Key	Reaction	$\left J(z=0.50~km)\right.$	J(z = 42.67 km)
$j_{O_2 \to O}$	$O_2 + h\nu \longrightarrow O + O$	2.95 E-10	5.16E-09
$j_{O_2 \to O(^1D)}$	$O_2 + h\nu \longrightarrow O + O(^1D)$	0	0
$j_{CO_2 \to O}$	$CO_2 + h\nu \longrightarrow CO + O$	3.79E-12	1.02E-10
$j_{CO_2 \to O(^1D)}$	$CO_2 + h\nu \longrightarrow CO + O(^1D)$	0	0
$j_{O_3 \to O(^1D)}$	$O_3 + h\nu \longrightarrow O_2 + O(^1D)$	3.12E-03	4.09E-03
$j_{O_3 \to O}$	$O_3 + h\nu \longrightarrow O_2 + O$	5.22E-04	6.86E-04
j_{H_2O}	$H_2O + h\nu \longrightarrow H + OH$	1.28E-10	4.67 E-08
$j_{H_2O_2}$	$H_2O_2 + h\nu \longrightarrow OH + OH$	3.93E-05	5.26E-05
j_{HO_2}	$HO_2 + h\nu \longrightarrow O + OH$	2.40E-04	3.20E-04

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The 1-D photochemistry model code used to construct this work has been frozen and stored on Zenodo, (Taysum, 2020a).

The datasets containing the atmospheric parameters and tracer mixing ratio profiles constructed from the Mars Climate Database v5.3 are also stored on Zenodo, (Taysum, 2020b).

All output files produced by the 1-D model used in this work, and plotting routines used to construct the figures and extract numerical data from the files, are stored on Zenodo, (Taysum, 2020c).

The TUV model source code used to construct the J-value look-up tables can be acquired through the url https://www2.acom.ucar.edu/modeling/tropospheric-ultravioletand-visible-tuv-radiation-model.

The Mars Climate Database v5.3 source code used to create the offline tables for atmospheric parameter and long-lived tracer vmr's for the 1-D model here can be acquired through the url http://www-mars.lmd.jussieu.fr/mars/access.html , requiring a request to be made to the researchers listed on the site.

679 References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes,

Table B3. Functions and constants used by the $R-O_2$ permutation reaction handling scheme extracted from the CAABA/MECCA v4.0 box model.

	CAABA/MECCA v4.0 Reaction Rate Parameters			
Key	Formula	Notes and Citations		
	Radical Arrhen	ius Equations		
k_ch3o2 k_ch3ooh k_ch3co2h k_ro2ho2_1 k_ro2ho2_2	$\begin{array}{c} 1.03E\text{-}13^*\exp(365/\text{T})\\ 5.30E\text{-}12^*\exp(190/\text{T})\\ 4.00E\text{-}14^*\exp(850/\text{T})\\ 2.91E\text{-}13^*\exp(1300/\text{T})^*(1\ -\ \exp(\text{-}0.245^*1)\)\\ 2.91E\text{-}13^*\exp(1300/\text{T})^*(1\ -\ \exp(\text{-}0.245^*2)\)\end{array}$	$\begin{array}{l} CH_3O_2 \ Self\mbox{-reaction (R. Sander et al., 2019)} \\ CH_3OOH + OH \ Reaction (R. Sander et al., 2019) \\ CH_3CO_2H + OH \ Reaction (R. Sander et al., 2019) \\ RO_2 + HO_2 \ (One \ carbon \ atom) \ (R. Sander et al., 2019) \\ RO_2 + HO_2 \ (Two \ carbon \ atoms) \ (R. Sander et al., 2019) \end{array}$		
	Arrhenius Equations for	H Abstraction by OH		
k_s k_t k_rohro k_roohro k_co2h kdec	$\begin{array}{c} 4.50\text{E-}18^{*}\text{T}^{2*}\text{exp}(253./\text{T})\\ 2.12\text{E-}18^{*}\text{T}^{2*}\text{exp}(696/\text{T})\\ 2.10\text{E-}18^{*}\text{T}^{2*}\text{exp}(-85/\text{T})\\ 0.60^{*}\text{k_ch3ooh}\\ 0.7^{*}\text{k_ch3co2h}\\ 1.00\text{E6} \end{array}$	(Taraborrelli, 2010; R. Sander et al., 2019) (Taraborrelli, 2010; R. Sander et al., 2019) (Atkinson et al., 2006; R. Sander et al., 2019)		
	Updated Rate Constants f	or $RO_3 + HO_2$ Reactions		
kapho2	$5.20E-13^{*}exp(980/T)^{*}1.865$	(Groß et al., 2014; R. Sander et al., 2019)		
	Arrhenius Equations for	Permutation Reactions		
k_ro2soro2 k_ro2rco3 k_ro2poro2	$\begin{array}{c} 2^{*}(7.70\text{E-}15^{*}\text{exp}(1330/\text{T})^{*}\text{k_ch3o2})^{0.5} \\ 4.00\text{E-}12^{*}\text{exp}(500/\text{T}) \\ 2^{*}7.50\text{E-}14^{*}\text{exp}(500/\text{T}) \end{array}$	(R. Sander et al., 2019)(R. Sander et al., 2019)(R. Sander et al., 2019)		
	Substituen	t Factors		
f_soh f_sooh f_pch2oh f_tooh f_to f_co f_cho f_co2h	3.44 8.00 1.29 8.00 2.68 8.15 0.55 1.67	(Taraborrelli, 2010; R. Sander et al., 2019) (Taraborrelli, 2010; R. Sander et al., 2019)		
	Branching Ratios for F	$RO_2 + HO_2$ Reactions		
rco3_o3 rco3_oh rco3_ooh rchoch2o2_oh rcoch2o2_oh rcoch2o2_ooh	$\begin{array}{c} 0.10 \\ 0.69 \\ 0.21 \\ 0.10 \\ 0.15 \\ 0.85 \end{array}$	(Groß et al., 2014; R. Sander et al., 2019) (Groß et al., 2014; R. Sander et al., 2019) (Groß et al., 2014; R. Sander et al., 2019) (R. Sander et al., 2019) (R. Sander et al., 2019) (R. Sander et al., 2019) (R. Sander et al., 2019)		

Table B4. Chemical reactions and rate coefficients involved in the oxidation of CH_4 used in our 1-D photochemistry model. Bimolecular rate coefficient units are cm³ molec⁻¹ s⁻¹. ^{*a*} are three-body reactions with values taken with atmospheric number density complying to temperatures of T = 298 K and pressures of 660 Pa. ^{*b*} are unimolecular rate coefficients with units s⁻¹.

	Me	thane Reaction Scheme		
Key	Reaction	Formula	Rate at T = 298 K $$	Reference
cab_1	$CH_4 + OH \longrightarrow CH_3 + OH$	1.85E-20exp(2.82LOG(T) - 987./T)	6.40E-15	(R. Sander et al., 2019)
cab_2	$CH_4 + O \longrightarrow 0.51 * CH_3 + 0.51 * OH$ +0.49 * $CH_3O + 0.49 * H$	$6.03\text{E-}18(\text{T}^{2.17})\text{exp}(\text{-}3619/\text{T})$	7.50E-18	(R. Sander et al., 2019)
cab_3	$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M$	k_3rd(7.00E-31, 3., 1.80E-12, -1.1)	$1.14\text{E-}13~^{a}$	(R. Sander et al., $2019)$
cab_4	$CH_3 + O_3 \longrightarrow 0.956 * HCHO + 0.956 * H + 0.044 * CH_3O + O_2$	5.10E-12exp(-210/T)	2.52E-12	(R. Sander et al., 2019) $$
cab_5	$\begin{array}{l} CH_3 + O \longrightarrow 0.83 * HCHO + 0.83 * H \\ + 0.17 * CO + 0.17 * H_2 + 0.17 * H \end{array}$	1.30E-10	1.3E-10	(R. Sander et al., 2019)
cab_6	$CH_3O_2 + HO_2 \longrightarrow CH_3OOH + O_2$	3.8E-13exp(780/T) /(1 + 1/(498exp(1160/T))))	5.21E-12	(R. Sander et al., 2019)
cab_7	$CH_3O_2 + HO_2 \longrightarrow HCHO + H_2O + O_2$	$3.8\text{E}-13\exp(780/\text{T})$ /(1 + 498exp(-1160/T)))	4.67E-13	(R. Sander et al., $2019)$
cab_8	$CH_3O_2 + R - O_2 \longrightarrow CH_3O + 0.5 * O_2$	2×7.40E-13exp(-520/T)	2.59E-13	(R. Sander et al., 2019) $$
cab_9	$CH_3O_2 + R - O_2 \longrightarrow 0.5 * HCHO$ +0.5 * $CH_3OH + 0.5 * O_2$	$2 \times (k_ch3o2 - 7.40E-13exp(-520/T))$	4.43E-13	(R. Sander et al., 2019)
cab_{10}	$CH_3O_2 + O_3 \longrightarrow CH_3O + O_2 + O_2$	2.90E-16exp(-1000/T)	1.01E-17	(R. Sander et al., 2019)
cab_{11}	$CH_3O_2 + OH \longrightarrow CH_3O + HO_2$	1.40E-10	1.40E-10	(R. Sander et al., 2019) (R. Sander et al., 2019)
cab_{12}	$CH_3O_2 + O \longrightarrow CH_3O + O_2$ $CH_2OH + OH \longrightarrow 0.85 * HCHO$	4.30E-11	4.30E-11	(R. Sander et al., 2019)
cab_{13}	$+0.85 * HO_2 + 0.15 * CH_3O + H_2O$	$6.38E-18(T^2)exp(144/T)$	9.19E-13	(R. Sander et al., 2019)
cab_{14}	$CH_3OOH + OH \longrightarrow 0.6 * CH_3O_2 + 0.4 * HCHO + 0.4 * OH + H_2O$	k_ch3ooh_oh	1.00E-11	(R. Sander et al., 2019)
cab_{15}	$CH_3O + O_2 \longrightarrow HO_2 + HCHO$	1.30E-14exp(-633/T)	1.55E-15	(R. Sander et al., 2019)
cab_{16}	$CH_3O + O_3 \longrightarrow CH_3O_2 + O_2$	2.53E-14	2.53E-14	(R. Sander et al., 2019)
cab_{17}	$CH_3O + O \longrightarrow 0.75 * CH_3 + 0.75 * O_2$ +0.25 * $HCHO + 0.25 * OH$	2.50e-11	2.50E-11	(R. Sander et al., 2019) $$
cab_{18}	$HCHO + OH \longrightarrow HCO + H_2O$	5.50E-12exp(-125/T)	3.60e-12	(S. Sander et al., 2011)
cab_{19}	$HCHO + HO_2 \longrightarrow HOCH_2O_2$	9.70E-15exp(625/T)	7.90E-14	(R. Sander et al., 2019)
cab_{20}	$HCHO + O \longrightarrow HCO + OH$	2.99E-11exp(-1529/T)	1.77E-13	(Herron, 1988)
cab_{21}	$HCO + O \longrightarrow CO + OH$	5.00E-11	5.00E-11	(Baulch et al., 1992)
cab_{22}	$HCO + CH_3 \longrightarrow CH_4 + CO$	4.40E-11	4.40E-11	(S. Mulenko, 1987)
cab_{23}	$HCO + CH_3 \longrightarrow CH_3CHO$	4.42E-11	4.42E-11	(S. A. Mulenko, 1980)
cab_{24}	$HCO + HCO \longrightarrow HCHO + CO$	4.48E-11	4.48E-11	(Friedrichs et al., 2002)
cab_{25}	$HCO + OH \longrightarrow CO + H_2O$	1.69E-10	1.69E-10	(Baulch et al., 1992)
cab_{26}	$HCO + O_2 \longrightarrow CO + HO_2$	5.20E-12	5.20E-12	(S. Sander et al., 2011)
cab_{27}	$HCO + H \longrightarrow CO + H_2$	1.83E-10	1.83E-10	(Friedrichs et al., 2002)
cab_{28}	$HOCH_2O_2 \longrightarrow HCHO + HO_2$	2.40E12exp(-7000/T)	150.89	(R. Sander et al., 2019)
cab_{29}	$HOCH_2O_2 + HO_2 \longrightarrow 0.5 * HOCH_2OOH + 0.5 * HCOOH + 0.2 * OH + 0.2 * HO_2 + 0.3 * H_2O + 0.8 * O_2$	5.6E-15exp(2300/T)	1.26E-12	(R. Sander et al., 2019)
cab_{30}	$HOCH_2O_2 + R - O_2 \longrightarrow HCOOH + HO_2$	2×(k_ch3o2×5.50E-12) ^{0.5}	2.78E-12	(R. Sander et al., 2019)
cab_{31}	$\begin{array}{l} HOCH_2O_2+R-O_2 \longrightarrow 0.5*HCOOH \\ +0.5*HOCH_2OH+0.5*O_2 \end{array}$	$2 \times (k_ch_{302} \times 5.70E-14 \times exp(750/T))^{0.5}$	9.95E-13	(R. Sander et al., 2019)
cab_{32}	$HCOOH + OH \longrightarrow CO_2 + HO_2 + H_2O$	2.94E-14exp(786/T) + 9.85E-13exp(-1036/T)	4.42E-13	(R. Sander et al., 2019)
cab_{33}	$HOCH_2OOH + OH \longrightarrow HOCH_2O_2$	k_roohro	6.02E-12	(R. Sander et al., 2019)
cab_{34}	$HOCH_2OOH + OH \longrightarrow HCOOH + H_2O + OH$	k_rohro + k_s×f_soh×f_sooh	2.59E-11	(R. Sander et al., 2019)
cab_{35}	$HOCH_2OH + OH \longrightarrow HO_2 + HCOOH + H_2O$	$2 \times k$ _rohro + k_s $\times f$ _soh ²	1.13E-11	(R. Sander et al., 2019)
cab_{107}	$CH_3 + OH + M \longrightarrow CH_3OH + M$	$2.5 \times dens \times 2.48 E\text{-}27 exp(298./t)^{3.8}$	9.92E-10	(Fagerstrm et al., 1994)

Table B5. Chemical reactions and rate coefficients involved in the oxidation of C_2H_6 used in our 1-D photochemistry model. Bimolecular rate coefficient units are cm³ molec⁻¹ s⁻¹. ^{*a*} are three-body reactions with values taken with atmospheric number density complying to temperatures of T = 298 K and pressures of 660 Pa. ^{*b*} are unimolecular rate coefficients with units s⁻¹.

	Ethane Reaction Scheme			
Key	Reaction	Formula	Rate at T = 298 K $$	Reference
cab_{36}	$C_2H_6 + OH \longrightarrow C_2H_5 + H_2O$	7.66E-12exp(-1020/T)	2.50E-13	(S. Sander et al., 2011)
cab_{37}	$C_2H_6 + O \longrightarrow C_2H_5 + OH$	2.21E-15(T/298) ^{6.5} exp(-132/T)	1.42E-15	(Cohen & Westberg, 1991)
cab ₃₈	$CH_3 + CH_3 + M \longrightarrow C_2H_6$	Details in (Cody et al., 2003)	5.12E-11 a	(Cody et al., 2003)
cab ₃₉	$C_2H_5 + O_2 + M \longrightarrow C_2H_5O_2$	2.5×1.50E-28(298/1) ^o ×dens	0.02E-11 "	(S. Sander et al., 2011) (Dabia & Banaan, 1001)
cab ₄₀	$C_2H_5 + C_2H_5 \longrightarrow C_2H_4 + C_2H_6$ $C_2H_5 + O_2 \longrightarrow C_2H_4 + HO_2$	2.01E-12 1.90E-14	2.01E-12 1.90E-14	(S Sander et al. 2011)
cabio	$C_2H_5 + O_2 \longrightarrow C_2H_4 + HO_2$ $C_2H_7 + H \longrightarrow CH_2 + CH_2$	7.95E-11exp(-132/T)	5.11E-11	(Pratt & Wood 1984)
cab ₄₂	$C_2H_5O_2 + HO_2 \longrightarrow C_2H_5OOH + O_2$	7.50E-13exp(700/T)	7.86E-12	(R. Sander et al., 2019)
1	$C_2H_5O_2 + RO_2 \longrightarrow 0.8 * CH_3CHO + 0.6 * HO_2$	0(7 COT 14%1 -1 2 -0)0.5	9.07E 19	(D. C., J., et al. 2010)
cab ₄₄	$+0.2 * C_2 H_5 OH + O_2$	2(7.00E-14 K_Ch302)	3.27E-13	(n. Sander et al., 2019)
cab_{45}	$C_2H_5OOH + HO_2 \longrightarrow C_2H_5OOH + O_2$	k_roohro	6.02E-12	(R. Sander et al., 2019)
cab_{46}	$C_2H_5OOH + OH \longrightarrow CH_3CHO + OH$	k_s*t_sooh	7.47E-12	(R. Sander et al., 2019)
cab_{47}	$C_2H_5OH + OH \longrightarrow 0.95 * C_2H_5O_2 + 0.95 * HO_2$ +0.05 * HOCH ₂ CH ₂ O ₂ + H ₂ O	3.00E-12exp(20/T)	3.21E-12	(R. Sander et al., 2019)
1	$HOCH_2CH_2O_2 + RO_2 \longrightarrow 0.6 * HOCH_2CH_2O$	0*(7.20E 14(1000/TE)*1	1 77E 10	(D. C., J., et al. 2010)
cab ₄₈	$+0.2 * HOCH_2CHO + 0.2 * ETHGLY$	2 (1.80E-14exp(1000/1) K_cn302)	1.77E-12	(R. Sander et al., 2019)
cab_{49}	$HOCH_2CH_2O_2 + HO_2 \longrightarrow HYETHO2H$	1.53E-13exp(1300/T)*(1-k_rchohch2o2_oh)	1.08E-11	(R. Sander et al., 2019)
cab ₅₀	$HOCH_2CH_2O_2 + HO_2 \longrightarrow HOCH_2CH_2O + OH$	1.53E-13exp(1300/1)*k_rchohch2o2_oh	1.20E-12 0.40E-15	(R. Sander et al., 2019) (D. Sander et al., 2019)
cab ₅₁	$HOCH_2CH_2O + O_2 \longrightarrow HO_2 + HOCH_2CHO$	0.00E-14exp(-500/1) 0.5E13orm(.5088/T)	9.46E-15 1.78E5 b	(R. Sander et al., 2019) (P. Sander et al., 2010)
cab ₅₂	$ETHGLY + OH \longrightarrow HOCH_{0}CHO + HO_{0} + H_{0}O$	2^{k} s ^{*f} soh ^{*f} pch2oh \pm 2^{k} rohro	8.57E-19	(R. Sander et al., 2019) (R. Sander et al., 2019)
cab ₅₃	$HYETHO2H + OH \longrightarrow HOCH_2OHO + HO2 + H_2O$	k roohro	6.02E-12	(R. Sander et al., 2019)
cab ₅₅	$HYETHO2H + OH \longrightarrow HOCH_2CHO + OH + H_2O$	k_s*f_sooh*f_pch2oh	9.64E-12	(R. Sander et al., 2019)
cab ₅₆	$HYETHO2H + OH \longrightarrow HOOCH_2CHO + HO_2 + H_2O$	k_s*f_soh*f_pch2oh + k_rohro	4.29E-12	(R. Sander et al., 2019)
cab_{57}	$CH_3CHO + OH \longrightarrow CH_3C(O) + H_2O$	4.40E-12exp(365/T)*0.95	1.42E-11	(R. Sander et al., 2019)
cab_{58}	$CH_3CHO + OH \longrightarrow HCOCH_2O_2 + H_2O$	4.40E-12exp(365/T)*0.05	7.48e-13	(R. Sander et al., 2019)
cab_{59}	$CH_3CHO + HO_2 \longrightarrow CH_3CHOHO_2$	3.46E12exp(-12500/(1.98*T)) / (2.24E2C*	4.77E-22	(R. Sander et al., 2019)
anh	$CH_{-}CHO + HCOOH \rightarrow CH_{-}CHOH + HCOOH$	$(1.17E + 10*T^{2.209})$ orp $(-556/(1.087T))$	1.24E 14	(P. Sandor et al. 2010)
cabe	$CH_{2}CHOH + OH \longrightarrow HCOOH + OH + HCHO$	(1.1712-19 1)exp(=550/(1.5571)) 4 30E-11	4.30E-11	(R. Sander et al., 2019) (R. Sander et al., 2019)
caber	$CH_2CHOH + OH \longrightarrow HOCH_2CHO + HO_2$	2.40E-11	2.40E-11	(R. Sander et al., 2019)
cab ₆₃	$CH_2CHOH + HCOOH \longrightarrow CH_3CHO + HCOOH$	(4.67E-26*T ^{3.286})exp(-556/(T*1.987))	2.47E-18	(R. Sander et al., 2019)
cab_{64}	$CH_3CHOHO_2 \longrightarrow CH_3CHO + HO_2$	3.46E12exp(-12500/(T*1.98))	2.18E3 ^b	(R. Sander et al., 2019)
cab ₆₅	$CH_3CHOHO_2 + HO_2 \longrightarrow 0.5 * CH_3CHOHOOH$	5.60E-15exp(2300/T)	1.26E-11	(R. Sander et al., 2019)
1	$+0.3 * CH_3COOH + 0.2 * CH_3 + 0.2 * HCOOH + 0.2 * OH + O_2$	1 2	0.0017 19	(D. G
cab ₆₆	$CH_3CHOHO_2 + RO_2 \longrightarrow CH_3 + HCOOH + OH$ $CH_2COOH + OH \longrightarrow CH_2 + CO_2 + H_2O$	4.00E-14exp(850/T)	9.08E-13 6.93E-13	(R. Sander et al., 2019) (R. Sander et al., 2019)
cabee	$CH_{2}CHOHOOH + OH \longrightarrow CH_{2}COOH + OH$	$k t^{*f} tooh^{*f} toh + k rohro$	4 19E-11	(R. Sander et al., 2019) (R. Sander et al. 2019)
cabeo	$CH_2CHOHOOH + OH \longrightarrow CH_2CHOHO_2$	k roohro	6.02E-12	(R. Sander et al., 2019)
cab ₇₀	$CH_3C(O) + O_2 + M \longrightarrow CH_3C(O)OO + M$	5.10E-12(1 - 1/(1 + 9.48E-18*dens*2.5))	4.04E-12 ^a	(R. Sander et al., 2019)
cab ₇₁	$CH_3C(O) + O_2 + M \longrightarrow OH + HCHO + CO + M$	5.10E-12/(1 + 9.48E-18*dens*2.5))	1.06E-12 ^a	(R. Sander et al., 2019)
cab_{72}	$CH_3C(O)OO + HO_2 \longrightarrow OH + CH_3 + CO_2$	5.20E-13exp(980/T)*1.507*0.61	1.28E-11	(R. Sander et al., 2019)
cab_{73}	$CH_3C(O)OO + HO_2 \longrightarrow CH_3C(O)OOH$	5.20E-13exp(980/T)*1.507*0.23	4.83E-12	(R. Sander et al., 2019)
cab ₇₄	$CH_3C(O)OO + HO_2 \longrightarrow CH_3COOH + O_3$	5.20E-13exp(980/T)*1.507*0.16	3.36E-12	(R. Sander et al., 2019) (D. Sander et al., 2010)
cab ₇₅	$CH_3C(O)OO + RO_2 \longrightarrow CH_3 + CO_2$ $CH_2C(O)OO + RO_2 \longrightarrow CH_2COOH$	k_ro2co3*0.1	1.95E-11 2.14E-12	(R. Sander et al., 2019) (P. Sander et al., 2019)
cab ₇₆	$CH_3C(O)OOH + OH \longrightarrow CH_3C(O)OO + H_0O$	k roohro	6.02E-12	(R. Sander et al., 2019) (R. Sander et al., 2019)
1	$HCOCH_2O_2 + RO_2 \longrightarrow 0.6 * HCHO + 0.6 * CO + 0.6 * HO_2$	1	0.02E 10	(D. C., J., et al. 2010)
cab ₇₈	$+0.2 * GLYOX + 0.2 * HOCH_2CHO$	k_ro2poro2	8.03E-12	(R. Sander et al., 2019)
cab ₇₉	$HCOCH_2O_2 + HO_2 \longrightarrow HOOCH_2CHO$	k_ro2ho2_2*rcoch2o2_ooh	7.52E-12	(R. Sander et al., 2019) (B. Sander et al., 2010)
cab ₈₀	$HCOCH_2O_2 + HO_2 \longrightarrow HCHO + CO + HO_2 + OH$	2 10E 120mm(240/T)	1.33E-12 0.70E-19	(R. Sander et al., 2019) (B. Sander et al., 2010)
cab ₈₁	$GLIOX + OH \longrightarrow HCOCO + H_2O$ $HCOCO \longrightarrow HCO + CO$	3.10E-12exp(340/1) 1.40E12exp(-3150/T)	3.54E7 b	(Orlando & Tyndall 2001)
cab ₈₂	$HCOCO + O_2 \longrightarrow HCOCO_2$	$5.00F-12^{*3}.2^{*}exp(-550/T)$	2.53E-12	(B. Sander et al., 2019)
cab_{84}	$HCOCO + O_2 \longrightarrow OH + CO + CO_2$	5.00E-12(1 - 3.2exp(-550/T))	2.47E-12	(R. Sander et al., 2019)
cab ₈₅	$HOOCH_2CHO + OH \longrightarrow HCOCH_2O_2 + H_2O$	k_roohro	6.02E-12	(R. Sander et al., 2019)
cab_{86}	$HOOCH_2CHO + OH \longrightarrow HCHO + CO + OH + H_2O$	0.8*8.00E-12	6.40E-12	(R. Sander et al., 2019)
cab_{87}	$HOOCH_2CHO + OH \longrightarrow GLYOX + OH + H_2O$	0.55*k_s*f_sooh*f_cho	2.26E-12	(R. Sander et al., 2019)
cab ₈₈	$HOCH_2CHO + OH \longrightarrow HOCH_2CO + H_2O$	0.8*8.00E-12	6.40E-12	(R. Sander et al., 2019)
cab ₈₉	$HOCH_2CHO + OH \longrightarrow HOCHCHO + H_2O$	0.2*8.00E-12	1.60E-12	(R. Sander et al., 2019) (D. Sander et al., 2019)
cab ₉₀	$HOCHCHO \rightarrow GLYOX + HO_2$ $HOCHCO + O_2 + M \rightarrow HOCHCO_2 + M$	KGec $5.10E 19*(1 - 1/(1 + 1.85E 18*done*9.5))$	1.00E0 9.17E 19.4	(R. Sander et al., 2019) (P. Sander et al., 2019)
caboo	$HOCH_2CO + O_2 + M \longrightarrow HOCH_2CO_3 + M$ $HOCH_2CO + O_2 + M \longrightarrow OH + HCHO + CO_2 + M$	$5.10E-12^{\circ}(1 + 1.85E-18^{\circ}dens^{\circ}2.5)$	8.89E-12 a	(R. Sander et al., 2019) (R. Sander et al., 2019)
cab ₉₂	$HOCH_2CO_3 + RO_2 \longrightarrow HCHO + CO_2 + HO_2$	k_ro2rco3*0.9	1.93E-11	(R. Sander et al., 2019)
cab ₉₄	$HOCH_2CO_3 + RO_2 \longrightarrow HOCH_2CO_2H$	k_ro2rco3*0.1	2.14E-12	(R. Sander et al., 2019)
cab_{95}	$HOCH_2CO_3 + HO_2 \longrightarrow HCHO + OH + HO_2 + CO_2$	kapho2*rco3_oh	9.25E-12	(R. Sander et al., 2019)
cab_{96}	$HOCH_2CO_3 + HO_2 \longrightarrow HOCH_2CO_3H$	kapho2*rco3_ooh	2.82E-12	(R. Sander et al., 2019)
cab_{97}	$HOCH_2CO_3 + HO_2 \longrightarrow HOCH_2CO_2H + O_3$	kapho2*rco3_o3	1.34E-12	(R. Sander et al., 2019)
cab_{98}	$HOC n_2 CO_2 n + On \longrightarrow 0.09 * HCHO + 0.91 * HCOCO_2 H + HO_2 + H_2O$	$k_co2h + k_s*f_soh*f_co2h$	5.50E012	(R. Sander et al., 2019)
cab_{99}	$HCOCO_2H + OH \longrightarrow CO + HO_2 + CO_2 + H_2O$	$k_co2h + k_t*f_o*f_co2h$	2.66E-11	(R. Sander et al., 2019)
cab_{100}	$HOCH_2CO_3H + OH \longrightarrow HOCH_2CO_3 + H_2O$	k_roohro	6.02E-12	(R. Sander et al., 2019)
cab_{101}	$HOCH_2CO_3H + OH \longrightarrow HCOCO_3H + HO_2$	k_s*f_soh*f_co2h	5.37E-12	(R. Sander et al., 2019)
cab_{102}	$HCOCO_3H + OH \longrightarrow HCOCO_3 + H_2O$	k_roohro	6.02E-12	(R. Sander et al., 2019)
cab ₁₀₃	$HCOCO_2 + RO_2 \longrightarrow CO + HO_2 + CO$ $HCOCO_2 + RO_2 \longrightarrow CO + HO_2 + CO$	k_t~t_o^t_co2h k_ro2rco2*0.0	2.65E-11 1.03E-11	(R. Sander et al., 2019) (B. Sander et al., 2010)
cab ₁₀₄	$HCOCO_3 + RO_2 \longrightarrow CO + RO_2 + CO_2$ $HCOCO_2 + RO_2 \longrightarrow HCOCO_2 H + O_2$	k ro2rco3*0 1	2.14F=12	(R. Sander et al., 2019) (R. Sander et al. 2010)
cab ₁₀₆	$HCOCO_3 + HO_2 \longrightarrow HO_2 + CO + CO_2 + OH$	kapho2	1.34E-11	(R. Sander et al., 2019)

Table B6. Organic photolytic reactions used within the 1-D photochemistry submodule. Values (s⁻¹) are interpolated from an offline look-up table constructed by a modified TUV (Madronich et al., 2002) model with respect to CO₂ and O₃ column abundances overheard, temperature, optical opacity and solar zenith angle. Values displayed are extracted for a solar zenith angle of 0°, $L_S = 251^{\circ}$ (perihelion).

Key	Reaction	$\left J(z=0.50~\mathrm{km})\right.$	$\left J(z=42.67~\mathrm{km})\right.$	J(z = 69.81 km)
$j_{CH_4 \rightarrow CH_3}$	$CH_4 + h\nu \longrightarrow CH_3 + H$	0.00	0.00	8.12E-10
$j_{CH_4 \rightarrow {}^1CH_2}$	$CH_4 + h\nu \longrightarrow^1 CH_2 + H_2$	0.00	0.00	1.63E-9
$j_{CH_4 \rightarrow {}^3CH_2}$	$CH_4 + h\nu \longrightarrow {}^3CH_2 + H + H$	0.00	0.00	1.53E-10
$j_{CH_4 \rightarrow CH}$	$CH_4 + h\nu \longrightarrow CH + H_2 + H$	0.00	0.00	1.95E-10
j_{CH_3OOH}	$CH_3OOH + h\nu \longrightarrow CH_3O + OH$	2.23E-5	2.90E-5	2.97E-5
$j_{HCHO \rightarrow HCO}$	$HCHO + h\nu \longrightarrow HCO + H$	3.54E-5	4.62E-5	4.74E-5
$j_{HCHO \rightarrow CO}$	$HCHO + h\nu \longrightarrow H_2 + CO$	3.71E-5	4.88E-5	5.01E-5
j_{CH_3OH}	$CH_3OH + h\nu \longrightarrow CH_3O + H$	1.59E-7	1.12E-6	1.64E-6
$j_{C_2H_6}$	$C_2H_6 + h\nu \longrightarrow Products$	0.00	0.00	2.39E-9
$j_{CH_3CHO \rightarrow CH_3}$	$CH_3CHO + h\nu \longrightarrow CH_3 + HCO$	2.43E-5	3.40E-5	3.44E-5
$j_{CH_3CHO \rightarrow CH_4}$	$CH_3CHO + h\nu \longrightarrow CH_4 + CO$	5.46E-6	6.80E-6	6.81E-6
j_{HOCH_2OOH}	$HOCH_2OOH + h\nu(+O_2) \longrightarrow HCOOH$ $+ HO_2 + OH$	4.43E-5	5.43E-5	5.43E-5
incan and nac	$HOCH_CHO + bu \longrightarrow CH_O + HCO$	4.08F 5	5.04F 5	5 05F 5
JHOCH ₂ CHO→HCO	$HOCH_2CHO + h\nu \longrightarrow CH_2OH + CO$	4.00E-0	6.07E 6	6.09E 6
$JHOCH_2CHO \rightarrow CO$	$HOCH_2CHO + h\nu \longrightarrow CH_3OH + CO$	4.311-0	0.0712-0	0.091-0
$j_{HOCH_2CHO \rightarrow OH}$	$HCOCH_2O_1 + OH$	3.44E-6	4.25E-6	4.26E-6
$j_{Glyox \rightarrow HCO}$	$Glyoxal + h\nu \longrightarrow HCO + HCO$	7.84E-5	8.49E-5	8.5E-5
$j_{Glyox \rightarrow H_2}$	$Glyoxal + h\nu \longrightarrow H_2 + CO + CO$	1.90E-5	2.19E-5	2.20E-5
$j_{Glyox \rightarrow HCHO}$	$Glyoxal + h\nu \longrightarrow HCHO + CO$	2.79E-5	3.13E-5	3.14E-5
$j_{CH_{3}COOH}$	$CH_3COOH + h\nu \longrightarrow CH_3 + COOH$	7.77E-6	9.43E-6	9.44E-6
	$CH_3C(O)OOH + h\nu \longrightarrow CH_3$	3 85F 5	4 73F 6	4 75F 5
JCH ₃ C(O)OOH	$+OH + CO_2$	3.00L-0	4.101-0	4.161-0
	Prox	cies		
Key	Reaction	P1	oxy	Source
$j_{HOCH_2CO_3H}$	$HOCH_2CO_3H + h\nu \longrightarrow HCHO + HO2 + OH + CO2$	2 јсн	300H	(R. Sander et al., 2014)
j_{HCOCO_2H}	$\begin{array}{c} HCOCO_2H + h\nu \longrightarrow 2HO_2 \\ +CO + CO_2 \end{array}$	$3.95 \times j_H$	$CHO \rightarrow CO$	(Kuhlmann et al., 2003)
<i>ј</i> сн ₃ сноноон	$\begin{array}{c} CH_{3}CHOHOOH+h\nu \longrightarrow CH_{3} \\ +HCOOH+OH \end{array}$	jсн	300H	(R. Sander et al., 2014)
$j_{Hyetho2h}$	$Hyetho2h + h\nu \longrightarrow HO_2 +CO + OH + CO_2$	$j_{CH_3OOH} + j_H$ $+j_{HOCH}$ $+j_{HOCH}$	$HOCH_2CHO \rightarrow HCO$ $H_2CHO \rightarrow CO$ $H_2CHO \rightarrow OH$	(R. Sander et al., 2014)
j_{HCOCO_3H}	$HCOCO_3H + h\nu \longrightarrow HO_2 + CO + OH + CO2$	j_{Hy}	etho2h	(R. Sander et al., 2014)
<i>јноосн₂сно</i>	$\begin{array}{c} HOOCH_2CHO + h\nu \longrightarrow HCHO + OH \\ +HO2 + CO \end{array}$	I j _{Hy}	etho2h	(R. Sander et al., 2014)

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