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► **To cite this version:**

L. Lara, E. Lellouch, M. Gonzalez, R. Moreno, M. Rengel. A time-dependent photochemical model for Titan's atmosphere and the origin of H₂O. *Astronomy and Astrophysics - A&A*, 2014, 566, pp.A143. 10.1051/0004-6361/201323085 . hal-02611789

HAL Id: hal-02611789

<https://hal.science/hal-02611789>

Submitted on 3 Nov 2022

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A time-dependent photochemical model for Titan's atmosphere and the origin of H₂O[★]

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Received 19 November 2013 / Accepted 17 April 2014

ABSTRACT

Context. Titan's stratosphere contains oxygen compounds (CO, CO₂, and H₂O), implying an external source of oxygen whose nature is still uncertain. Recent observations from the *Herschel* Space Observatory using the HIFI and PACS instruments and the *Cassini*/CIRS, as well as steady-state photochemical modeling indicate that the amounts of CO₂ and H₂O in Titan's stratosphere may imply inconsistent values of the OH/H₂O input flux, and that the oxygen source is time-variable.

Aims. We attempt to reconcile the H₂O and CO₂ observed profiles in Titan's atmosphere by using an updated photochemical scheme and developing several time-dependent scenarios for the influx/evolution of oxygen species.

Methods. We use a time-dependent photochemical model of Titan's atmosphere to calculate effective lifetimes and the response of Titan's oxygen compounds to changes in the oxygen input flux. Two variants for the C-H-O chemical network are considered. We investigate a time-variable Enceladus source and the evolution of material delivered by a cometary impact.

Results. We find that the effective lifetime of H₂O in Titan's atmosphere is only a factor of six shorter than that of CO₂ and exceeds 10 yr below 200 km. A time-variable Enceladus source, involving a decrease by a factor of 5–20 in the OH/H₂O flux over the last few centuries, shows promise in explaining the relative CO₂/H₂O profiles. However, if the previous measurements from the *Herschel* Space Observatory are representative of Titan's atmospheric water, an additional H₂O loss to the haze term is needed to bring the model in full agreement with the data. In an alternate situation, CO₂ production following a cometary impact that occurred at least 220–300 yr ago can in principle explain the CO₂ “excess” in Titan's stratosphere, but this scenario is highly unlikely, given the estimates of the impact rate at Titan.

Key words. planets and satellites: atmospheres – planets and satellites: individual: Titan – planets and satellites: composition

1. Introduction

The presence of water vapor in the stratosphere of the outer planets, as established by ISO, has raised the question of the origin of external oxygen in these reducing environments. While the gross similarity of the H₂O fluxes into the four giant planets (Feuchtgruber et al. 1997) might have been taken as evidence that micrometeorite ablation is the dominant source, recent observations, especially using the *Herschel* Space Observatory (*Herschel* hereafter), have revealed a different picture. These datasets outline the role of recent cometary impacts in delivering H₂O, CO and CO₂ to Jupiter and CO in Neptune and possibly Saturn and that of Enceladus' activity in feeding Saturn's upper atmosphere with water vapor (see Cavalié et al. 2013, and references therein).

Following the original detection by ISO (Coustenis et al. 1998), the presence of water vapor has been recently revived by measurements of the H₂O vertical profile by both *Cassini*/CIRS (Cottini et al. 2012) and *Herschel*/PACS and *Herschel*/HIFI (Moreno et al. 2012) at Titan. These studies differed significantly in the amounts of H₂O implied by typically a factor of 4–5 at 115 km. Based on photochemical modeling, Moreno et al. (2012) found that the modeled CO₂ abundance at 100–200 km

is too small by a factor of ~10 compared to the observed value of 10–20 ppb when the H₂O influx is adjusted to match their water profile. Noting that the atmospheric lifetimes of CO₂ and H₂O are very different, Moreno et al. (2012) proposed that the discrepancy could be solved by invoking a variable input flux over timescales of tens to hundreds of years and tentatively favored Enceladus' plume activity as the source of Titan's external oxygen.

Most recently, Dobrijevic et al. (2014) presented a fully coupled oxygen-nitrogen-hydrocarbon model, in which a number of reactions had been updated or added since the previous models by Hörst et al. (2008) and Moreno et al. (2012); in particular, reactions between N- and O-bearing species were considered. They confirmed the essential conclusion of Moreno et al. (2012) in that the measured H₂O profile is inconsistent with the CO₂ abundance, although the disagreement was reduced to a factor of 4. Dobrijevic et al. (2014) found that reconciliation was possible if water abundances reported by Cottini et al. (2012) are correct instead; although in this situation and for an Enceladus source, their model tended to overpredict the thermospheric abundance of H₂O when compared to the globally averaged upper limit determined by Cui et al. (2009). Dobrijevic et al. (2014) also find that the deposition altitude of the OH/H₂O flux (750 km, which is representative of micrometeorite ablation, vs. the top of the atmosphere, which is characteristic

* Tables 1–3 are available in electronic form at <http://www.aanda.org>

of an Enceladus source) influences the flux required to reproduce the observed H₂O and CO₂ profiles and the abundance of secondary N-O and H-N-O species.

In this work, by means of a time-dependent photochemical model, we explore in more details the scenario of a variable oxygen source at Titan to see whether it is a plausible explanation to the “H₂O/CO₂ puzzle”. We consider both the H₂O profiles derived from *Cassini*/CIRS (Cottini et al. 2012) and from *Herschel* (Moreno et al. 2012). In addition, we study a scenario when Titan might have suffered a cometary impact in the past by bringing oxygen species into its atmosphere.

2. Model description

The number density n at altitude z for every constituent i at time t is solved by means of the usual continuity equations in spherical geometry:

$$\frac{\partial n_i}{\partial t} = P_i - n_i l_i - \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \Phi_i), \quad (1)$$

where Φ_i can be expressed as

$$\Phi_i = -n_i D_i \left(\frac{1}{n_i} \frac{\partial n_i}{\partial z} + \frac{1 + \alpha_i}{T} \frac{\partial T}{\partial z} + \frac{1}{H_i} \right) - n_i K \left(\frac{1}{n_i} \frac{\partial n_i}{\partial z} + \frac{1}{T} \frac{\partial T}{\partial z} + \frac{1}{H} \right). \quad (2)$$

The variable n_i , P_i , and l_i are the number density, volumic production rate, and volumic specific loss rate, and $r = R_0 + z$, where $R_0 = 2575$ km and z runs from 34 to 1432 km with an altitude bin size of 1 km. The parameter D_i is the molecular diffusion coefficient, T is temperature, H_i and H are the individual and atmospheric scale heights, $K(z)$ is the eddy diffusion coefficient, and, α_i is the thermal diffusion coefficient. The equations are solved for methane CH₄, methyl radical CH₃, acetylene C₂H₂, ethylene C₂H₄, ethane C₂H₆, methyl acetylene CH₃C₂H, propane C₃H₈, diacetylene C₄H₂, atomic hydrogen H, molecular hydrogen H₂, carbon monoxide CO, carbon dioxide CO₂, O(³P), formyl HCO, formaldehyde H₂CO, hydroxyl OH, CH, C₂, C₄H, C₃H₅, C₂H, ¹CH₂, ³CH₂, C₂H₃, C₂H₅, C₄H₂^{*}, C₄H₃, O(¹S), O(¹D), CH₃O, and CH₃CO.

We use a fully implicit finite difference scheme (unconditionally stable) with a variable Δt time step to accommodate the large range of characteristic times (i.e., turbulent transport, molecular diffusion, and chemical times for all the species).

The model, which originally derives from Lara et al. (1996), has been updated in several ways. First we include new reaction rates for the hydrocarbons (see Table 1). Second, for the chemical network involving oxygen species, we consider two schemes: (i) the one from (Hörst et al. 2008, hereafter H08), which was also used by (Moreno et al. 2012, see Table 2); and (ii) a modified C-H-O chemical scheme, which results from common reactions in Dobrijevic et al. (2014) and in Hörst et al. (2008) that are updated with rate coefficients in Dobrijevic et al. (2014), and additional reactions from Dobrijevic et al. (2014) that only involve the hydrocarbons and oxygen species listed above. Specifically, this means that we ignore reactions coupling N and O chemistry. This is justified by the fact that we are primarily interested by the profiles of CO₂ and H₂O and not the abundances of secondary N-O-H species. In particular, the reaction OH + N(⁴S) in the reaction scheme coupling N and O species (which in the C-H-N-O chemistry by Dobrijevic et al. (2014) is important above 1000 km to produce NO) only represents 0.003% of

the OH column integrated loss in the C-H-O chemical network for typical OH and N(⁴S) vertical profiles. Regarding water, the main additional loss term that involves nitrogen is H₂O + N(²D), but this only accounts for 0.85% of the total water loss rate given typical profiles of H₂O and N(²D). Reactions for this simplified chemical scheme (hereafter L14), with regard to Dobrijevic et al. (2014) are listed in Table 3.

Finally, compared to Lara et al. (1996), a more recent treatment of the UV transmission in the haze layer is considered. For this, we have adopted the results shown in Fig. 2 of Krasnopolsky (2009), which in fact do not noticeably differ from the approximation seen in Yung et al. (1984) as used in Lara et al. (1996) and in Moreno et al. (2012).

Here we retain the same treatment for the condensation processes, as in Lara et al. (1996), and adopt the eddy diffusion coefficient (K_2) from Moreno et al. (2012). Following Hörst et al. (2008), the O(³P) flux is introduced in the model in a layer with a peak at 1100 km. The magnitude of the O(³P) flux normally drives the CO abundance. However, due to its extremely long lifetime (several 10⁸ yr), reaching a chemical balance on CO needs a long integration time (e.g. Dobrijevic et al. 2014). Instead the CO mixing ratio is prescribed hereat its observed value, 5.1×10^{-5} (Gurwell 2004), at the model’s lower boundary; the abundance vertical profile is then computed in the model, and the O(³P) flux is then unimportant for determining the CO₂ and H₂O profiles. As detailed below, we investigate the sensitivity of the results to form (OH vs. H₂O) and the deposition profile of the water influx.

Boundary conditions at 34 km are set as follows: for condensable species, the mixing ratio is the maximum value allowed by the saturation laws, which is zero supersaturation; for non-condensable species, either they are in local photochemical equilibrium and the number density is computed as the quotient of the production and specific loss, or they have a maximum flux through the lower boundary. At 1432 km, only H and H₂ are allowed to escape according to the Jeans formulation, whereas the other species are in diffusive equilibrium (excluding OH/H₂O in the case that they have an inward flux due to the Enceladus plume activity).

The thermal profile used for our computation is a combination of (i) the temperatures measured by Huygens/HASI (Fulchignoni et al. 2005) in the troposphere at altitudes between 0–140 km; (ii) the disk-averaged *Cassini*/CIRS stratospheric temperatures (Vinatier et al. 2010) at altitudes between 140–500 km; (iii) the *Cassini*/INMS retrieved temperatures (i.e. 155 K as average, de La Haye et al. (2007)) at altitudes between 1000–1500 km; and (iv) a decreasing temperature from 165 K to 155 K at altitudes between 500 and 1000 km.

Our study aims at reproducing (i) the H₂O vertical profiles in Moreno et al. (2012) and Cottini et al. (2012) with both chemical schemes, for H08 and L14; and (ii) the CO₂ stratospheric abundance from *Cassini*/CIRS data (de Kok et al. 2007).

3. OH versus H₂O external source

Both Hörst et al. (2008) and (Moreno et al. 2012, who considered the H08 chemical scheme) concluded that the OH vs. H₂O form of the water input is unimportant when fitting the stratospheric water abundance, since a balance is established between OH and H₂O, due to the photolysis of water and reactions between OH and CH₃ or OH and CH₄ recycling water. They also found that fluxes required to reproduce a given H₂O profile are independent on the precise deposition profile (i.e., deposition at the top of the atmosphere as appropriate or in a Chapman

Table 4. Steady-state models results for an OH and H₂ flux at the top of the atmosphere.

Observed profile	Chemical network	OH flux (cm ⁻² s ⁻¹)	H ₂ O (cm ⁻² s ⁻¹)	O(³ P) flux (cm ⁻² s ⁻¹)	CO ₂ mixing ratio at 150 km
<i>S_a</i> (Moreno et al. 2012)	H08	2.4 × 10 ⁵	0	1.6 × 10 ⁶	6.2 × 10 ⁻¹⁰
<i>S_a</i> (Moreno et al. 2012)	L14	3.2 × 10 ⁵	0	1.6 × 10 ⁶	8.7 × 10 ⁻¹⁰
<i>S_a</i> (Moreno et al. 2012)	L14	0	2.6 × 10 ⁵	1.6 × 10 ⁶	8.7 × 10 ⁻¹⁰
CIRS (Cottini et al. 2012)	H08	9.0 × 10 ⁵	0	1.0 × 10 ⁶	2.5 × 10 ⁻⁹
CIRS (Cottini et al. 2012)	L14	1.2 × 10 ⁶	0	1.6 × 10 ⁶	3.3 × 10 ⁻⁹
CIRS (Cottini et al. 2012)	L14	0	9.8 × 10 ⁵	1.6 × 10 ⁶	3.3 × 10 ⁻⁹

layer near 750 km). On the other hand, Dobrijevic et al. (2014) found large variations in the required H₂O/OH flux depending on its H₂O vs. OH form and on its altitude deposition. For example, Table 2 of Dobrijevic et al. (2014) shows that a given flux produces ~33% more H₂O in Titan's atmosphere for meteoritic ablation near 750 km (cases "IM1" and "IM4"), when it is deposited in the form of H₂O compared to the case where it is deposited as OH. The difference becomes larger in the case of water deposition at the top of the atmosphere (cases "IE1" and "IE2"), where a OH flux (compared to H₂O flux) that is twice as large is needed to produce the same amount of H₂O.

We re-examined these issues with the new treatment of the UV transmission within the haze and the new chemical network (L14). For this, we computed steady-state solutions by fine-tuning the OH/H₂O influx to match the available observations (HIFI+PACS in Moreno et al. (2012) and Cassini/CIRS by Cottini et al. (2012)). Table 4 summarizes the required fluxes to match the H₂O determinations from *Herschel* and Cassini/CIRS by using the two sets of chemistry and water influx in the form of either OH or H₂O. (Only cases of deposition at the top of the atmosphere are summarized in Table 4.)

Although we do find with our simplified L14 scheme values that are similar to Dobrijevic et al. (2014), Table 4 indicates that an influx in the form of H₂O entering Titan's atmosphere is more "efficient" at producing H₂O in Titan's atmosphere than an OH flux; the difference is only about 20% (vs. a factor ~2 in Dobrijevic et al. 2014). Moreover, for a given form of deposition (OH or H₂O), we do not find any significant difference between the required fluxes as a function of deposition profile, as the associated Titan H₂O profiles for a given flux and the two scenarios of deposition profiles are identical up to 750 km. In contrast, the profiles start to diverge above this altitude as seen in Figs. 12 and 13 of Moreno et al. (2012), so that measurements of the H₂O mole fraction in the upper atmosphere could help constrain the Enceladus in contrast to micrometeoroid ablation origin of the external flux. We are unsure of the cause of the discrepancy with Dobrijevic et al. (2014), and we do not understand why their required fluxes are so dependent on the altitude deposition profile. Indeed, we estimated that the non-inclusion of the N-O coupling has a negligible effect of the fluxes required to match a given H₂O profile above, and the latter authors do not explicitly show a case with the N-O chemistry turned off for comparison. Likely reasons of the discrepancy may be related to significantly different profiles of the C-H and C-H-N species profiles computed in (Dobrijevic et al. 2014, not shown therein) and ours.

4. Lifetimes

Moreno et al. (2012) could not simultaneously fit the stratospheric abundance of H₂O measured with *Herschel* and of CO₂ (de Kok et al. 2007) with the same OH and O(³P) flux. They proposed that the discrepancy could be solved by invoking a

time-variable input flux. They based their argument on the different atmospheric lifetimes of H₂O and CO₂. This had been already found by Wilson & Atreya (2004), who reported chemical lifetimes of 4.1 and 697 yr at 300 km for H₂O and CO₂. Moreno et al. (2012) obtained similar numbers (9 yr and 450 yr) for the "column-integrated" lifetime, which is defined by dividing the column density by the vertically-integrated chemical loss including photolysis. For CO₂, this lifetime was comparable to the vertical transport time down to the condensation level (360 yr). However, these approaches give either an estimate of the lifetime against chemical loss at some level or a global estimate of the atmospheric residence time of a species in the atmosphere, but they do not handle the fact that the time evolution of the atmospheric mixing ratios depends on both chemical and transport processes, which may show important variations with altitude.

To account for this, we first used our time-dependent model as described, to study the response of oxygen species to an abrupt change in the oxygen source rate. For this, we initialized the oxygen compounds to the steady state solution profiles obtained in the case of the OH Enceladus source (i.e. deposited at the top of the atmosphere) by considering the two variants of the oxygen chemistry (H08 and L14). The steady state OH fluxes required to match the H₂O *Herschel* profile are given in Table 4, and an O(³P) flux of 1.6 × 10⁶ cm⁻² s⁻¹ is used. Then, for each case, the oxygen sources are cut to zero and the oxygen species evolve with time. For each species, we define the altitude-dependent "effective lifetime" as the time after which the mixing ratio has decreased by a factor *e* at the considered altitude. This definition is clearly only approximate since the time evolution does not follow a simple exponential decay. Results for the H08 chemical network are shown in Fig. 1 for all oxygen species but CO (which has a very long lifetime at all levels). It has to be pointed out that the "effective lifetimes" for every species are approximately the same when using the H08 or the L14 chemical network.

For comparison, Fig. 2 shows the altitude-dependent lifetimes associated to the different processes considered in the model for some oxygen species (CO₂, H₂O, H₂CO, O(³P) and OH): photolysis, gas-gas chemical reactions (for which the lifetime is defined at each altitude *j* as the minimum of 1/*k*_{*i,j*}, *k* that represents all of the reactions consuming the species *i* at altitude *j*), molecular diffusion, and turbulent transport. For H₂O, the photolytic lifetime (which drives the overall chemical lifetime) increases from ~0.5 yr at the top of the atmosphere to ~10 yr at 200 km and further increases at lower levels. The ratio of the chemical lifetime of CO₂ to that of H₂O is a factor of 100 above 400 km. All these numbers are consistent with the above estimates of the "column-integrated" chemical lifetimes.

Nonetheless, the time evolution of the at a given level is more properly described by the effective lifetimes (Fig. 1). For H₂O, it increases regularly from ~0.1 yr at the top to 10 yr

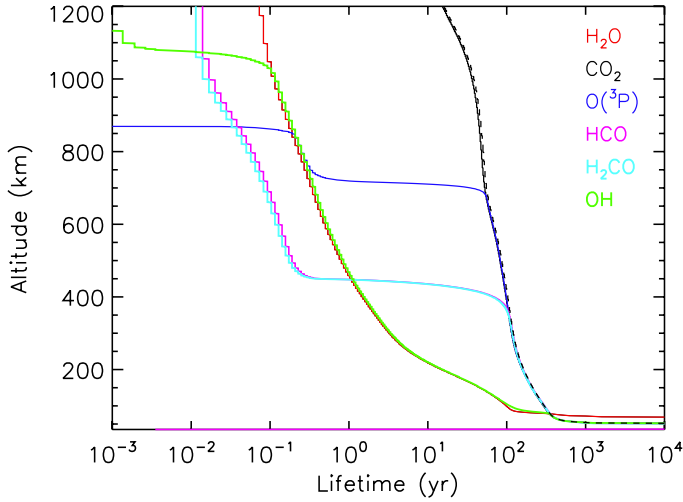


Fig. 1. Effective lifetimes (see text for definition) as a function of altitude for oxygen species. These are calculated for OH and O(³P) input fluxes of 2.4×10^5 and $1.6 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$, respectively, and the H08 chemical network. The effective lifetime for CO₂ for an enhanced input OH flux = $5.1 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ (needed to match the CO₂ profile) is also shown as a dashed black line.

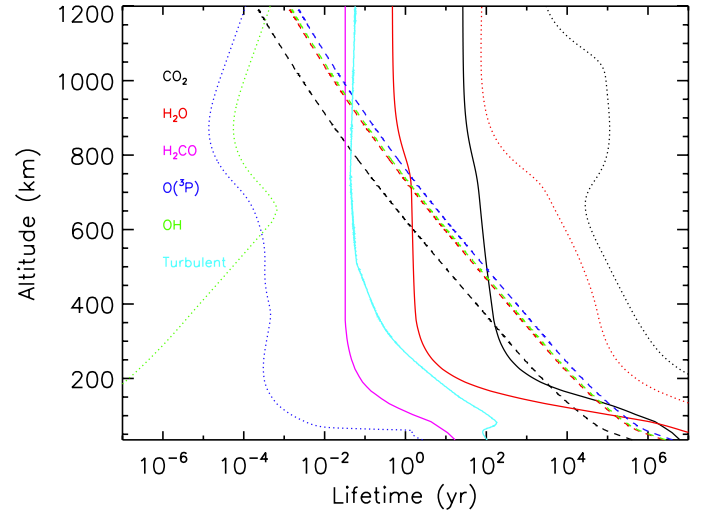


Fig. 2. Lifetimes for different processes. Solid lines: photolytic lifetime. Dotted lines: chemical (gas-gas) lifetime. Dashed lines: molecular diffusion timescale. (H_i^2/D_i). The characteristic time for turbulent transport (H^2/K) is also shown. This figure makes use of the H08 chemical scheme, where OH photolysis is not included, and H₂CO is only lost via photodissociation.

at 200 km and about 100 yr at 80 km (at deeper levels, H₂O is constrained to very small amounts by condensation, so the apparent “divergence” of the lifetime is not meaningful). For CO₂, the effective lifetime increases from 20 yr at the top of the atmosphere to 400 yr at ~80 km before entering in the condensation region. The OH lifetime is very short in the upper atmosphere (>1000 km) but it tracks that of H₂O from which it is photochemically produced below this altitude. Similarly, the lifetimes of O(³P) and HCO/H₂CO are short below 850 and 450 km and progressively increase to follow that of CO₂ below 700 and 400 km, respectively. For these four species, the long lifetimes in the lower atmosphere have, however, little significance because the involved amounts are very small. In addition to the altitude-dependent effective lifetime, it is useful to similarly define the column-averaged effective lifetime as the time after which the column density has decreased by a factor e . These column-average lifetimes are found to be 287 yr, 51 yr, 12 d, 10 d, 5 h, and 1 h for CO₂, H₂O, H₂CO, HCO, OH, and O(³P), respectively. The most important result for our purpose is that the effective lifetimes for CO₂ and H₂O differ by less than a factor of 6, regardless of the photochemical scheme and the initial profile to which time-evolution is applied.

5. Evolution of the H₂O and CO₂ profiles under changes of the input flux

Running the time-dependent model shows that all species except CO, CO₂, and H₂O decrease to molar fractions $<10^{-12}$ in less than 10 yr upon an abrupt cut-off of the oxygen input fluxes. While the shape of the CO₂ profile is conserved as the CO₂ abundance slowly declines with time, the H₂O profile strongly evolves. As a consequence of the quick altitude-varying lifetime, the H₂O depletion proceeds much more rapidly at upper levels, causing a local maximum (“kink”) of the H₂O mixing ratio in the 125–160 km altitude range to appear after ~10 yr. This behavior occurs for both the H08 and L14 chemical networks, and initial water profiles in agreement with either *Herschel* or *Cassini/CIRS* data. Figure 3 shows the evolution of the CO₂ and

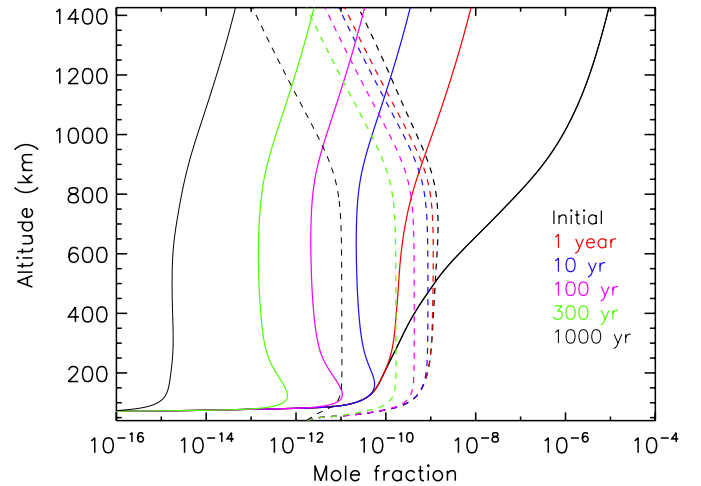


Fig. 3. Time-evolution of oxygen species 1, 10, 100, 300 and 1000 yr after the oxygen sources have been abruptly cut-off. Profiles are initialized at steady-state conditions for O(³P) and OH input fluxes at 1.6×10^6 and $2.4 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$, respectively, matching the H₂O profile of [Moreno et al. \(2012\)](#). Solid lines refer to H₂O, and dashed lines refer to CO₂.

H₂O profiles for initial conditions that match the S_a profile in [Moreno et al. \(2012\)](#) and adopt the H08 chemistry.

5.1. Time-variable input fluxes

Building on this, we considered a simple scenario for the time evolution of the oxygen fluxes to test the hypothesis of a time-variable Enceladus source being responsible for the “inconsistent” H₂O and CO₂ abundances. Essentially, we assume that the input fluxes have been strong enough in the past to explain the observed CO₂ and that they have decreased exponentially since some recent time. We describe the history of the OH flux as

- for $t < \text{current epoch} - t_0$: $\Phi(\text{OH}) = \Phi_0(\text{OH})$;
- for $t > \text{current epoch} - t_0$: $\Phi(\text{OH}) = \Phi_0(\text{OH}) \times \exp(-t/\tau)$,

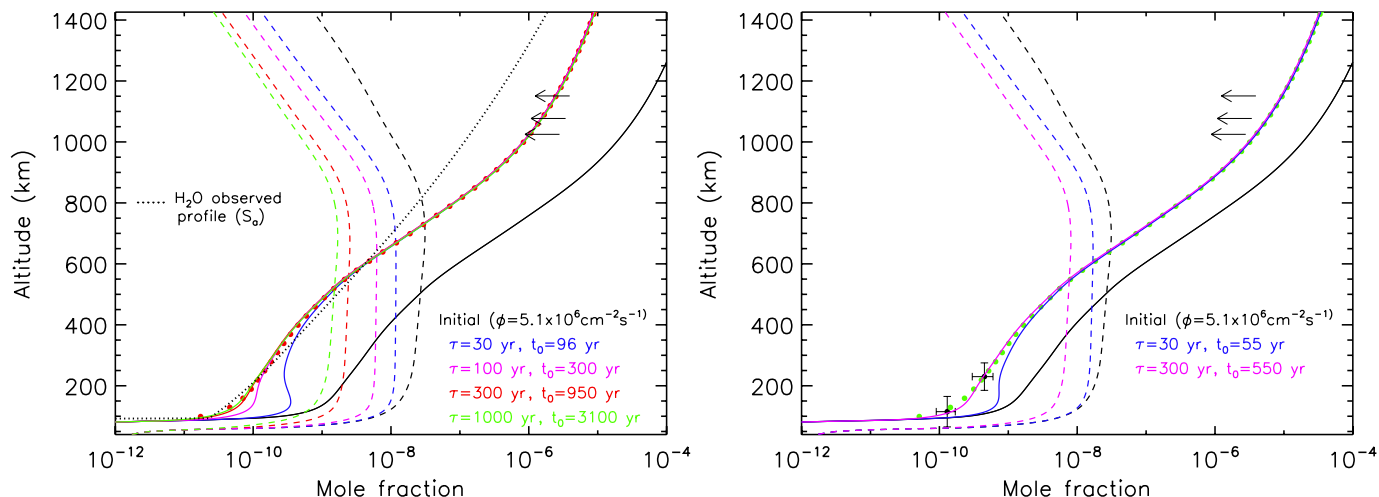


Fig. 4. H₂O (solid lines) and CO₂ (dashed lines) profiles in a time-dependent Enceladus source model, as compared to observations, making use of the H08 chemical scheme. *Left panel:* results aimed at fitting the H₂O observed with *Herschel*. The profiles are initialized at their steady-state values for a OH flux of $5.1 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ (black curves). The different curves correspond to evolution with four different combinations of τ and t_0 . The red circles show the H₂O profile in the ($\tau = 30 \text{ yr}$, $t_0 = 96 \text{ yr}$) case calculated in presence of an additional loss of H₂O to the haze (see text). *Right panel:* results aimed at fitting the H₂O observed with *Cassini/CIRS*. The black curves correspond to the steady state profiles obtained with an OH flux of $5.1 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$. Evolution of these profiles for two different (τ , t_0) combinations are shown, as well as the resulting H₂O profile, when a loss to the haze is taken into account for the ($\tau = 30 \text{ yr}$, $t_0 = 55 \text{ yr}$) case (green dots). Upper limits on H₂O thermospheric abundance by Cui et al. (2009) are also shown as arrows.

where t is the time elapsed since the onset of the flux decline, which is assumed to have started t_0 yr before the current epoch. The model thus has three free parameters: (i) t_0 , the number of years in the past when the input fluxes have started to decrease; (ii) $\Phi_0(\text{OH})$, the input flux before it started to decrease; and (iii) τ , the characteristic time of the flux decline. Since we are modeling an Enceladus source, we assume that the O(³P) flux follows the same time dependence and fix the O(³P)/OH flux ratio to a constant value.

In the first step, we fixed $\Phi_0(\text{OH})$ at the value required to match the observed CO₂ mole fraction of 1.5×10^{-8} at 100–200 km in a steady-state situation. This $\Phi_0(\text{OH})$ flux depends slightly on the photochemical network, being $5.1 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ for H08 and $5.3 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ for L14. These values are 16–20 times larger than the steady-state flux needed to match the H₂O profile of Moreno et al. (2012) and 4–5.5 times larger than that required to match the H₂O profile of Cottini et al. (2012). In the middle/upper atmosphere (say above 300 km), the lifetime of H₂O is short, so that the H₂O mole fraction reacts to the “instantaneous” flux. This essentially constrains the flux to have declined by the above factors, which implies $t_0/\tau = 2.9\text{--}3.2$ if the water targeted profile is S_a in Moreno et al. (2012) and $t_0/\tau = 1.5\text{--}1.8$ if the H₂O abundance to be reproduced is from *Cassini/CIRS* data (Cottini et al. 2012). The value of τ (and hence t_0) remains to be adjusted. However, the CO₂ abundance, which reflects the input flux that is “smoothed” over ~ 300 yr, and the profile of H₂O below 300–400 km, tend to provide contradictory constraints. Short values of τ and t_0 are favored by CO₂, while the steep H₂O slope (i.e., the absence of a “kink” near 150 km) would rather point to long values of τ and t_0 . Figure 4 shows the profiles of H₂O and CO₂ for various (τ , t_0) combinations aimed at reproducing:

- (left panel): H₂O from *Herschel* (Moreno et al. 2012) and CO₂ from *Cassini/CIRS* observations (de Kok et al. 2007), and
- (right panel): H₂O and CO₂ from *Cassini/CIRS* observations (Cottini et al. 2012; de Kok et al. 2007).

In the first case (target H₂O profile = S_a from Moreno et al. (2012)), the ($\tau = 30 \text{ yr}$, $t_0 = 96 \text{ yr}$) combination permits to reproduce a CO₂ profile that closely agrees with its observed value, but the H₂O profile shows a marked local maximum and an abundance that is too large below 250 km. Conversely, for ($\tau = 1000 \text{ yr}$, $t_0 = 3100 \text{ yr}$), the H₂O profile is adequate, but CO₂ is underabundant by a factor of 10. Intermediate sets of parameters, such as ($\tau = 100 \text{ yr}$, $t_0 = 300 \text{ yr}$) or ($\tau = 300 \text{ yr}$, $t_0 = 950 \text{ yr}$), produce unsatisfactory compromises with a poor fit for both species.

The same general conclusion can be seen in the right panel of Fig. 4, where the target H₂O profile is now taken from Cottini et al. (2012). For ($\tau = 30 \text{ yr}$, $t_0 = 55 \text{ yr}$), the CO₂ stratospheric value is close to the measurements, but the water profile sharply overestimates the H₂O mixing ratio near 125 km. For ($\tau = 300 \text{ yr}$, $t_0 = 550 \text{ yr}$), H₂O is brought into agreement with *Cassini/CIRS* results, but CO₂ is considerably below observations.

As can be seen on the right panel of Fig. 4, the models tuned to match the H₂O abundance somewhat overestimate the upper limits (2.8×10^{-6} up to 3.9×10^{-6} in the 1025–1151 km region) from INMS (Cui et al. 2009). A similar problem was encountered by Dobrijevic et al. (2014) for an Enceladus source. We note, however, that Cui et al. (2009) report actual detections of H₂O on several inbound spectra with H₂O mixing ratios in the range $(0.4\text{--}3.4) \times 10^{-5}$ with a mean value of 1.2×10^{-5} . These mixing ratios would then be consistent with model predictions, so the resolution of this issue must await a clarification of the constraints from INMS. At any rate, we note that the H₂O thermospheric abundance is sensitive to the precise OH vs. H₂O and vertical deposition profile and might also be affected by reactions (not considered here) that couple the O and N chemistry. In contrast, these effects do not affect the H₂O and CO₂ stratospheric abundances.

The above models assumed an initial $\Phi_0(\text{OH})$ equal to the steady-state value needed to fit the CO₂ abundance. We explored alternative models with a higher value for $\Phi_0(\text{OH})$. Specifically

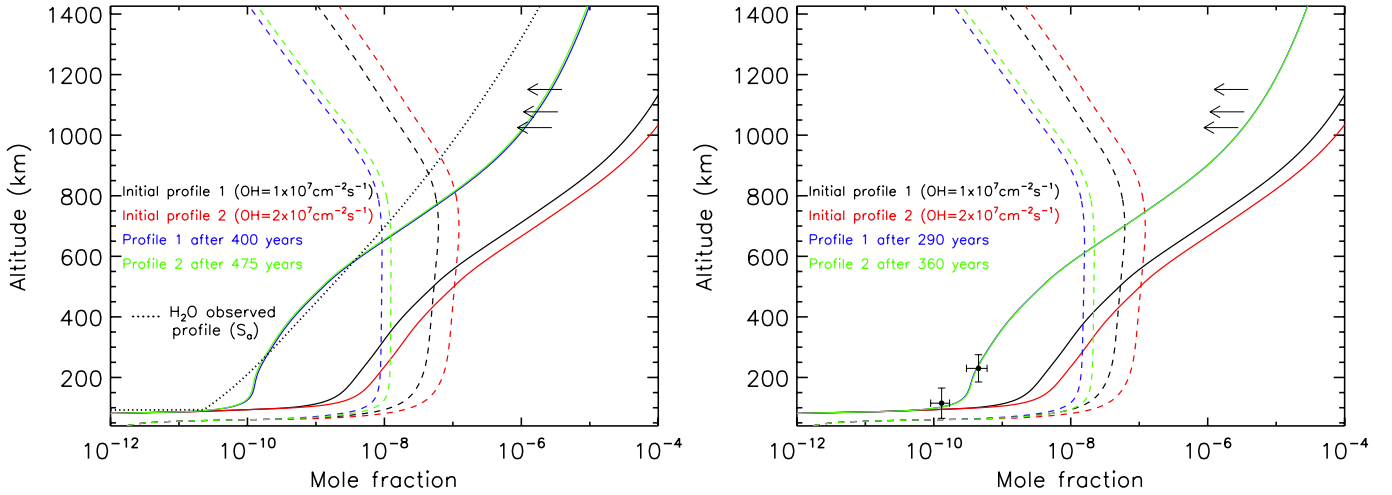


Fig. 5. H₂O (solid lines) and CO₂ (dashed lines) profiles in a time-dependent Enceladus source model (H08 chemistry) compared to the observed profile of H₂O from (i) *left panel*: *Herschel* (S_a profile from [Moreno et al. \(2012\)](#); and (ii) *right panel*: *Cassini/CIRS* ([Cottini et al. 2012](#)). Two initial conditions with different and enhanced OH input fluxes (1.0×10^7 in black lines and 2.0×10^7 cm⁻² s⁻¹ in red lines) are considered. Evolution times are adjusted so that the H₂O mole fraction above 300 km matches observations in the case of *Herschel* data and at 230 km in the case of *Cassini/CIRS*. The resulting (i.e., after t_0 yr of evolution) H₂O and CO₂ profiles are plotted with blue and green lines for the initial profiles 1 and 2, respectively (see text for more details). Upper limits on H₂O thermospheric abundance by [Cui et al. \(2009\)](#) are also shown as arrows.

Table 5. Evolution time t_0 required to match the *Herschel* or *Cassini/CIRS* H₂O profiles for both chemical schemes (H08 or L14).

$\Phi_0(\text{OH})$ (cm ⁻² s ⁻¹)	H08 chemical scheme		L14 chemical scheme	
	<i>Herschel</i> ^a	<i>Cassini/CIRS</i>	<i>Herschel</i> ^a	<i>Cassini/CIRS</i>
1.0×10^7	400	290	375	260
2.0×10^7	475	360	450	330

Notes. The time constant of the flux decline is $\tau = 100$ years. ^(a) Poor fit.

with the H08 chemical scheme, we considered two cases with initial fluxes of $\Phi_0(\text{OH}) = 1.0 \times 10^7$ and 2.0×10^7 cm⁻² s⁻¹, respectively, that then declined with a time constant $\tau = 100$ yr. The evolution time t_0 needed to match the H₂O *Herschel* abundance above 300 km altitude is 400 yr and 475 yr for the two cases, respectively. As shown in Fig. 5 (left panel), this scenario maintains larger CO₂ values compared to the $\tau = 100$ yr case shown in Fig. 4 (which had $t_0 = 300$ yr and $\Phi_0(\text{OH}) = 5.1 \times 10^6$ cm⁻² s⁻¹). The $\Phi_0(\text{OH}) = 2.0 \times 10^7$ cm⁻² s⁻¹ case yields CO₂ abundances that are essentially consistent with the observed $\sim 1.5 \times 10^{-8}$ value at 100–200 km. However, the corresponding H₂O profile still shows some “kink” below 200 km. Direct comparison of synthetic spectra with data from [Moreno et al. \(2012\)](#) indicates that it still overpredicts the PACS lines (which probe the 90–150 km range) by $\sim 50\%$ while the H₂O model correctly fits the HIFI observations.

On the other hand, the same approach provides a satisfactory match to the *Cassini/CIRS* H₂O measurements at 115 and 230 km. Continuing with the same chemical scheme, initial $\Phi_0(\text{OH})$ fluxes, and $\tau = 100$ yr, we find that the [Cottini et al. \(2012\)](#) H₂O profile can be reproduced with $t_0 = 290$ yr for $\Phi_0(\text{OH}) = 1.0 \times 10^7$ cm⁻² s⁻¹ and $t_0 = 360$ yr for $\Phi_0(\text{OH}) = 2.0 \times 10^7$ cm⁻² s⁻¹ (see Fig. 5, right panel). In both cases, the resulting CO₂ stratospheric profile agrees well with observations.

We performed the same exercise by using the alternate chemical network (L14). Keeping the characteristic time of the flux decline at $\tau = 100$ years, Table 5 summarizes the required values of the evolution time t_0 for the different cases. Similar behaviors

are obtained with the two sets of chemistry. We conclude that this family of solutions is not satisfactory if the targeted water profile is the one retrieved from *Herschel* data, whereas a more successful fit of *Cassini/CIRS* water and carbon dioxide is obtained by assuming considerably OH higher fluxes some centuries ago.

5.2. Loss to the haze

[Moreno et al. \(2012\)](#) speculated that the H₂O profile could be affected by an additional non-gaseous chemical loss, which can be a loss to the haze, as it seems to be the case for HCN ([McKay 1996](#); [Lara et al. 1999](#); [Vinatier et al. 2007](#)). [Moreno et al. \(2012\)](#) found that adding a loss term in the form of $L = k[\text{H}_2\text{O}]^{1.75}$ cm⁻³ s⁻¹ restricted to altitudes above 220 km would bring the model to the calculated H₂O profile in agreement with the *Herschel* observations. However, they discarded this option because it does not help reconcile in itself the H₂O and CO₂ profiles in the steady-state scenario considered in [Moreno et al. \(2012\)](#).

Nonetheless, in this time-dependent scenario, a loss to the haze potentially reduces the H₂O mole fraction in the lower stratosphere, as eliminates the H₂O “kink” near 150 km and recovers an H₂O profile in light with the *Herschel* observations. To illustrate this, here we come back to the short evolution case of Fig. 4 (left panel) (having $\Phi_0(\text{OH}) = 5.1 \times 10^6$ cm⁻² s⁻¹, $\tau = 30$ yr, $t_0 = 96$ yr), add a loss term of H₂O to the haze in the form $L = k[\text{H}_2\text{O}]^\beta$ cm⁻³ s⁻¹ at $z > 300$ km, which decreases with a -100 km scale height below 300 km. In a nominal case, we adopt $\beta = 1.75$ by analogy to results of HCN ([Lara et al. 1999](#)),

Table 6. Models with H₂O loss to the haze.

$\Phi_0(\text{OH})$ ($\text{cm}^{-2} \text{s}^{-1}$)	Chemical network	Target H ₂ O profile	(t_0, τ) (year)	(k, β)	CO ₂ mixing ratio at 150 km	H ₂ O integrated loss to the haze ($\text{cm}^{-2} \text{s}^{-1}$)
5.1×10^6	H08	<i>Herschel</i>	(96, 30)	($5.0 \times 10^{-16}, 2$)	9.3×10^{-9}	5.9×10^5
				($2.0 \times 10^{-14}, 1.75$)	9.2×10^{-9}	6.5×10^5
	<i>Cassini/CIRS</i>	(55, 30)	($1.5 \times 10^{-16}, 2$)	1.2×10^{-8}	2.2×10^5	
			($1.0 \times 10^{-14}, 1.75$)	1.2×10^{-8}	2.5×10^5	
5.3×10^6	L14	<i>Herschel</i>	(87, 30)	($5.0 \times 10^{-16}, 2$)	9.9×10^{-9}	6.1×10^5
				($2.0 \times 10^{-14}, 1.75$)	9.8×10^{-9}	6.8×10^5
	<i>Cassini/CIRS</i>	(45, 30)	($1.5 \times 10^{-16}, 2$)	1.2×10^{-8}	2.5×10^5	
			($1.0 \times 10^{-14}, 1.75$)	1.2×10^{-8}	2.8×10^5	

but solutions with different forms are possible. The red circles in the left panel of Fig. 4 show the resulting H₂O profile obtained with $k = 2 \times 10^{-14}$. This profile fully agrees with the empirical S_a profile of Moreno et al. (2012). Alternate functional dependences of L are possible; for example, $L = k'[\text{H}_2\text{O}]^2 \text{cm}^{-3} \text{s}^{-1}$ with $k' = 5 \times 10^{-16}$ at $z > 300$ km and similarly decreases below this altitude produces an identical fit. In these models, the total H₂O loss to the haze is $\sim 6 \times 10^5 \text{cm}^{-2} \text{s}^{-1}$.

For completeness, this study has been extended to the case of the H₂O *Cassini/CIRS* profile and also considers the two chemical schemes. Table 6 shows results of the (k, β) parameters and the total H₂O loss to the haze for the different cases.

As a conclusion, including a loss to the haze term in combination on with a time variable flux brings the modeled H₂O profile in agreement with available observations (Cottini et al. 2012; Moreno et al. 2012) for both of the chemical schemes used here, which maintains CO₂ stratospheric profiles in broad agreement with *Cassini/CIRS* data (de Kok et al. 2007).

6. Comet impact scenario

In this section, we investigate another alternative for the high CO₂/H₂O ratio in Titan's atmosphere: namely, the CO₂ that has built up from a relatively recent cometary impact. As shown from the Shoemaker-Levy 9 impacts on Jupiter in 1994, cometary impacts can deliver oxygen compounds to planets. In the Jupiter/SL9 case, shock chemistry at plume re-entry has produced CO and H₂O near the 0.1 mbar level (Lellouch et al. 1997, 2002), and both species have since then slowly diffused vertically and horizontally (see Moreno et al. 2003; Cavalié et al. 2013, and references therein). Furthermore, while CO is chemically stable, any newly injected H₂O is progressively photolysed to OH and converted to CO₂ by reaction with CO. The gas CO₂ was observed in 1997 in Jupiter (Lellouch et al. 2002) with a north-south asymmetry characteristic of a SL9-derived product (Lellouch et al. 2002). Based on coupled photochemical-horizontal transport modeling, the amount of carbon dioxide and latitudinal distribution could be explained if the material produced by the impacts has a H₂O/CO ratio of about 0.11 per volume. In Jupiter's atmosphere, the model further predicted that CO₂ produced in this manner would build up for about 50 yr after the impacts and then begin to decline due to its own photolysis. Comet impacts are also invoked to explain the abundance of CO in Neptune's stratosphere (Lellouch et al. 2005; Hesman et al. 2007) and possibly Saturn's (Cavalié et al. 2010).

We first examine the scenario for Titan in terms of the involved amounts. The CO₂ column density in Titan's atmosphere is $3.6 \times 10^{16} \text{cm}^{-2}$ which corresponds to 3.0×10^{34} molecules referred to the surface. Assuming full conversion of H₂O to CO₂

and using an initial H₂O/CO ratio of 0.1, this implies that the hypothetical comet delivered 3.0×10^{34} H₂O and 3.0×10^{35} CO molecules (i.e, a CO mass of 1.4×10^{13} g). Converting this CO mass into a comet size requires an assumption of the "CO yield" and the comet density. We use a 50% yield (Lellouch et al. 1997, 2005) and a 0.5 g cm⁻³ mass density. This gives a minimum $D = 0.475$ km comet diameter.

We then consider the time evolution of a "pure" cometary case, by first considering the constraints from the H₂O *Herschel* profile. The CO and H₂O mole fractions are initialized as q_{CO} and $q_{\text{H}_2\text{O}}$, which are taken as uniform above 300 km (0.1 mbar) and zero below this altitude. These values are considered as constant over the Titan globe. Thus the model is not initialized at comet impact, but a few years after when the species have been mixed horizontally and vertically above the 300 km range ($q = q_{\text{CO}}$). We impose $q_{\text{CO}} = 10 \times q_{\text{H}_2\text{O}}$, and these values are adjusted until the CO₂ mole fraction matches the observations after some evolution time t_{evol} . Figure 6 (left panel) shows two cases (both of which consider the H08 chemical network): (1) $q_{\text{CO}} = 6 \times 10^{-5}$, $t_{\text{evol}} = 300$ yr; and (2) $q_{\text{CO}} = 6 \times 10^{-4}$, $t_{\text{evol}} = 700$ yr. These two cases correspond to the deposition of 1.2×10^{36} and 1.2×10^{37} CO molecules implying a cometary diameter of 0.7 and 1.5 km ("small" and "large"), respectively, under the above assumptions on density and CO yield. Both cases produce roughly the same amount of CO₂; in contrast, a significantly larger amount of H₂O is present in the first case, although this amount of water is importantly below the *Herschel* observations in both cases. Case (1) represents the maximum amount of cometary H₂O that can be accommodated by the observed *Herschel* H₂O profile. This implies that the comet impact occurred at least 300 yr ago with a minimum comet diameter of 700 m. Older impacts are possible but require larger impactor sizes to maintain the same amount of CO₂.

The right panel of Fig. 6 shows similar models but are tailored to the *Cassini/CIRS* H₂O profile. The "large" comet case is unchanged, but the "small" comet case has values of $q_{\text{CO}} = 3 \times 10^{-5}$, $t_{\text{evol}} = 225$ yr. Indeed, the larger stratospheric abundance in the *Cassini/CIRS* H₂O profile can accommodate a larger residual cometary H₂O than the *Herschel* profile. This can be achieved by invoking a smaller and more recent impact (leading to the same CO₂ amount but a larger H₂O/CO₂ ratio after evolution). As it is clear in the right panel of Fig. 6, this case is close to the maximum value of cometary H₂O that can be tolerated by the observed *Cassini/CIRS* H₂O profile. This means that if the *Cassini/CIRS* H₂O profile is valid, the impact age could be as young as 225 years with the minimum size of 550 m. Again, older and larger impacts are possible.

We can also combine one of the above models with steady-state production of the oxygen species. This scenario thus

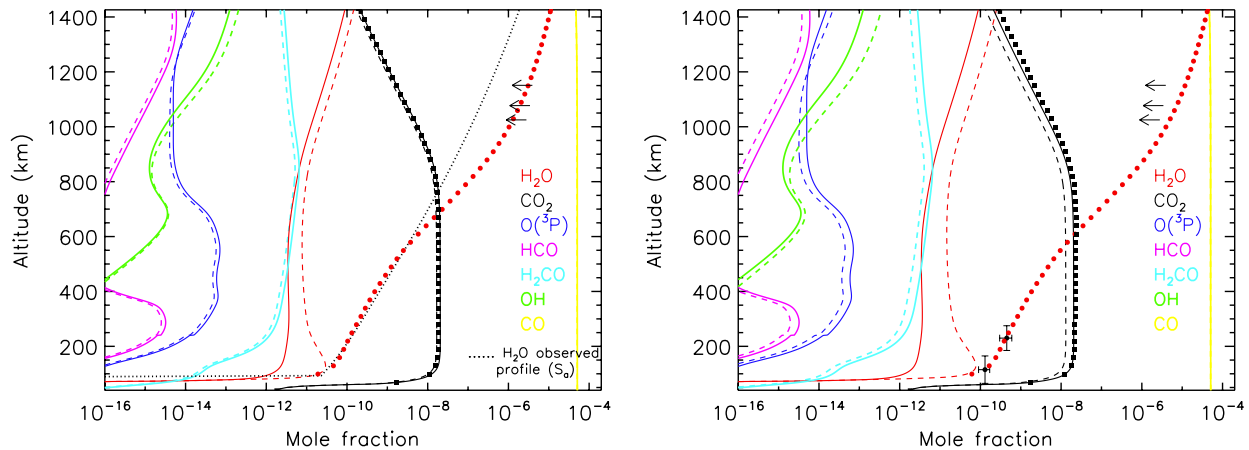


Fig. 6. Evolution of oxygen species after a cometary impact. Initial conditions correspond to deposition of CO and H₂O with uniform mixing ratios (with $q_{\text{CO}} = 10 q_{\text{H}_2\text{O}}$) above 300 km. *Left panel:* models suited to the *Herschel* H₂O profile (S_a from [Moreno et al. \(2012\)](#)). Dashed lines: “small comet” (initial $q_{\text{CO}} = 6 \times 10^{-5}$), evolution time $t_{\text{evol}} = 300$ yr. Solid lines: “large comet” (initial $q_{\text{CO}} = 6 \times 10^{-4}$), evolution time $t_{\text{evol}} = 700$ yr. The red circles and black squares show the H₂O and CO₂ for the combination of the “large comet” case with a steady OH influx of $2.4 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$. *Right panel:* models suited to the *Cassini/CIRS* H₂O profile [Cottini et al. \(2012\)](#). Dashed lines: “smaller comet” (initial $q_{\text{CO}} = 3 \times 10^{-5}$), evolution time $t_{\text{evol}} = 225$ yr. Solid lines: “large comet” (initial $q_{\text{CO}} = 6 \times 10^{-4}$), evolution time $t_{\text{evol}} = 700$ yr. The red circles and black squares show the H₂O and CO₂ for the combination of the “large comet” case with a steady OH influx of $9.0 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$. Upper limits on H₂O thermospheric abundance by [Cui et al. \(2009\)](#) are also shown as arrows.

depicts the current abundance of oxygen species as a result from the combination of a steady (Enceladus or micrometeorite) source and the evolution of a cometary “spike”. The steady source is primarily responsible for the H₂O abundance, while CO₂ is mostly the result of the comet impact. The dotted lines in Fig. 6 show the combination of the “large comet” above case with an Enceladus source (with a steady OH source rate of $2.4 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$ in the left panel and $9.0 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$ in the right panel). The resulting H₂O profiles after 700 yr evolution agree with *Herschel* and *Cassini/CIRS* observations, respectively, and the CO₂ profile is also fit.

The use of the alternate (L14) oxygen chemical scheme does not noticeably influence the results above. Matching the observations for the same model assumptions in terms of comet size and evolution time only requires a slight ($\leq 10\%$) increase of the Φ_{OH} that is provided by the steady Enceladus source. This is to be expected from Table 4, which shows the L14 oxygen chemical scheme to be slightly less efficient in producing atmospheric water.

While these models “technically” work, their main difficulty is in the plausibility of a recent impact at Titan. [Zahnle et al. \(2003\)](#) find that the number of impacts on Jupiter by 1.5 km or larger ecliptic comets is typically 0.005 per year. They further provide probabilities for ecliptic comet impacts relative to Jupiter for all outer planets and satellites. For Titan, this relative probability is given as 5.4×10^{-5} , which means that Titan is hit by a $D > 1.5$ km comet every ~ 4 million years on average. The size distribution of the cumulative impact rate is not very steep (slope parameter $b = 1-1.7$ in this size range, according to [Zahnle et al. 2003](#)), which means that the occurrence of a 0.5 km comet impact at Titan is only 3–6 times larger. We are still left with typical impact times of ~ 1 million years, which is probably fatal for this scenario.

7. Conclusions

We have explored Titan oxygen photochemistry by using a time-variable photochemical model and considering two variants for

the oxygen chemical schemes. We find that the effective lifetime of H₂O in Titan’s atmosphere exceeds 10 yr below 200 km, which is only a factor of six shorter than that of CO₂ when the column densities are averaged. As a consequence, solving the inconsistency between the OH/H₂O fluxes required matching the observed H₂O and CO₂ amounts, which is not straightforward and depends on the magnitude of the flux discrepancy. We find that if the [Cottini et al. \(2012\)](#) measurements are representative of Titan’s true H₂O profile, the factor about five in the discrepancy in flux can be solved by invoking a decrease by a factor of ten in the OH/H₂O flux (i.e., of Enceladus’ plume activity) over the last ~ 300 years. While the past activity of Enceladus is unconstrained, the fact that active plumes are currently not emitted along entire tiger stripes fractures and that thermal anomalies are not limited to fractures leaves open the possibility of a more extended and intense activity. If on the other hand, Titan’s water is even less abundant by about another factor of four as found by [Moreno et al. \(2012\)](#), we find that the time-dependent flux scenario is not in itself able to solve the problem and that another loss term for H₂O, such as a loss to the haze, has to be invoked.

Acknowledgements. This research has been supported by the Spanish Ministerio de Ciencia e Innovación under contract AyA 2009-08011 and Ministerio de Economía y Competitividad under contract AyA 2012-32237. We thank Ralph D. Lorenz for suggesting the comet impact scenario to us.

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Table 1. Hydrocarbon reactions.

	Reaction	Rate coefficient	Reference
R1a	${}^1\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$	9.24×10^{-11}	Langford et al. (1983)
R1b	${}^1\text{CH}_2 + \text{H}_2 \rightarrow {}^3\text{CH}_2 + \text{H}_2$	1.26×10^{-11}	Langford et al. (1983)
R2	${}^1\text{CH}_2 + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CH}_3$	6.0×10^{-11}	Böhland et al. (1985)
R3	$\text{CH} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	$3.96 \times 10^{-8} T^{-1.04} e^{-36.1/T}$	Canosa et al. (1997)
R4	$\text{CH} + \text{H}_2 + \text{M} \rightarrow \text{CH}_3 + \text{M}$	$k_0 = 8.75 \times 10^{-31} e^{524/T}$ $k_\infty = 8.3 \times 10^{-11}$	Moses et al. (2005) Fulle & Hippler (1997)
R5	$\text{H} + \text{CH}_3 + \text{M} \rightarrow \text{CH}_4 + \text{M}$	$k_0 = 1.7 \times 10^{-24} T^{-1.8}$ $k_\infty = 3.5 \times 10^{-10}$	Baulch et al. (1994)
R6	$\text{CH}_3 + \text{CH}_3 + \text{M} \rightarrow \text{C}_2\text{H}_6 + \text{M}$	$k_0 = 2.822 \times 10^{-3} T^{-8.749} e^{-985.4/T}$ $k_\infty = 9.3132 \times 10^{-11} e^{-1.519 \times 10^{-3} T}$	Cody et al. (2003); Lavvas et al. (2008)
R7	$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	$k_0 = 1.5 \times 10^{-29} T^{-1.3}$ $k_\infty = 1.0 \times 10^{-11}$	Tsang & Hampson (1986) Lavvas et al. (2008)
R8	$\text{H} + \text{C}_2\text{H}_2 + \text{M} \rightarrow \text{C}_2\text{H}_3 + \text{M}$	$k_0 = 2.6 \times 10^{-31}$ $k_\infty = 3.8 \times 10^{-11} e^{-1374/T}$	Baulch et al. (1992)
R9	$\text{H} + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$	3.30×10^{-11}	Monks et al. (1995)
R10	$\text{H}_2 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	$2.6 \times 10^{-13} e^{-2646/T}$	Fahr & Laufer (1995)
R11	$\text{H} + \text{C}_2\text{H}_4 + \text{M} \rightarrow \text{C}_2\text{H}_5 + \text{M}$	$k_0 = 2.15 \times 10^{-29} T^{-2} e^{-349/T}$ $k_\infty = 4.95 \times 10^{-11} e^{-1051/T}$	Baulch et al. (1994)
R12	$\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{CH}_3 + \text{CH}_3$	$7.95 \times 10^{-11} e^{-127/T}$	Pratt & Wood (1984)
R13	${}^3\text{CH}_2 + \text{H} + \text{M} \rightarrow \text{CH}_3 + \text{M}$	$k_0 = 3.4 \times 10^{-32} e^{736/T}$ $k_\infty = 7.3 \times 10^{-12}$	Moses et al. (2000)
R14	${}^3\text{CH}_2 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	7.0×10^{-11}	Tsang & Hampson (1986)
R15	${}^3\text{CH}_2 + \text{C}_2\text{H}_2 + \text{M} \rightarrow \text{CH}_3\text{C}_2\text{H} + \text{M}$	$k_0 = 6.0 \times 10^{-29} e^{1680/T}$ $k_\infty = 2.0 \times 10^{-12} e^{-3330/T}$	Böhland et al. (1988)
R16	$\text{C}_2\text{H} + \text{H} + \text{M} \rightarrow \text{C}_2\text{H}_2 + \text{M}$	$k_0 = 1.26 \times 10^{-18} e^{-721/T}$ $k_\infty = 3.0 \times 10^{-10}$	Tsang & Hampson (1986)
R17	$\text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}$	$5.58 \times 10^{-11} e^{-1443/T}$	Opansky & Leone (1996b)
R18	$\text{C}_2\text{H} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3$	$6.94 \times 10^{-12} e^{-250/T}$	Opansky & Leone (1996a)
R19	$\text{C}_2\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_5$	$5.1 \times 10^{-11} e^{-76/T}$	Murphy et al. (2003)
R20	$\text{C}_2\text{H} + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_2 + \text{H}$	1.3×10^{-10}	Vakhtin et al. (2001)
R21	$\text{CH}_3\text{C}_2\text{H} + \text{H} \rightarrow \text{CH}_3 + \text{C}_2\text{H}_2$	$9.62 \times 10^{-12} e^{-1560/T}$	Wagner & Zellner (1972)
R22	$\text{CH}_3\text{C}_2\text{H} + \text{H} + \text{M} \rightarrow {}^3\text{H}_5 + \text{M}$	$k_0 = 8.0 \times 10^{-24} T^{-2} e^{-1225/T}$ $k_\infty = 9.7 \times 10^{-12} e^{-1550/T}$	Yung et al. (1984) Wang et al. (2000)
R23	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2$	3.5×10^{-11}	Laufer & Fahr (2004)
R24	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 + \text{M} \rightarrow \text{C}_4\text{H}_6 + \text{M}$	$k_0 = 2.822 \times 10^{-3} T^{-8.749} e^{-985.4/T}$ $k_\infty = 9.5 \times 10^{-11}$	Lavvas et al. (2008) Laufer & Fahr (2004)
R25	$\text{C}_4\text{H} + \text{H}_2 \rightarrow \text{C}_4\text{H}_2 + \text{H}$	$1.20 \times 10^{-11} e^{-998/T}$	Lavvas et al. (2008)
R26	$\text{C}_4\text{H} + \text{CH}_4 \rightarrow \text{C}_4\text{H}_2 + \text{CH}_3$	$1.2 \times 10^{-11} e^{-491/T}$	Lavvas et al. (2008)
R27	$\text{C}_4\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_4\text{H}_2 + \text{C}_2\text{H}_5$	$5.1 \times 10^{-11} e^{-76/T}$	Lavvas et al. (2008)
R28	$\text{C}_4\text{H} + \text{H} + \text{M} \rightarrow \text{C}_4\text{H}_2 + \text{M}$	$k_0 = 1.26 \times 10^{-18} T^{-3.1} e^{-721/T}$ $k_\infty = 3.0 \times 10^{-10}$	Moses et al. (2000)
R29	$\text{CH}_4 + \text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_2 + \text{H}$	1.3×10^{-10}	Lavvas et al. (2008)
R30	$\text{C}_4\text{H} + \text{C}_4\text{H}_2 \rightarrow \text{C}_8\text{H}_2 + \text{H}$	$1.1 \times 10^{-10} e^{28/T}$	Moses et al. (2000)
R31	$\text{C}_2\text{H} + \text{C}_4\text{H}_2 \rightarrow \text{C}_6\text{H}_2 + \text{H}$	1.3×10^{-10}	Lavvas et al. (2008)
R32	${}^*\text{C}_4\text{H}_2 + \text{C}_4\text{H}_2 \rightarrow \text{C}_8\text{H}_2 + \text{H}_2$	1.5×10^{-10}	Zwier & Allen (1996)
R33	$\text{C}_4\text{H}_2 + \text{H} \rightarrow \text{C}_4\text{H}_3$	$1.4 \times 10^{-10} e^{-1184/T}$	Schwanebeck & Warnatz (1975); Nava et al. (1986)
R34a	$\text{C}_4\text{H}_3 + \text{H} \rightarrow \text{C}_4\text{H}_2 + \text{H}_2$	5.0×10^{-12}	Wang & Frenklach (1997)
R34b	$\text{C}_4\text{H}_3 + \text{H} \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_2$	1.5×10^{-11}	Wang & Frenklach (1997)
R35	$\text{C}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H} + \text{H}$	$1.77 \times 10^{-10} e^{-1469/T}$	Pitts et al. (1982)
R36	$\text{C}_2 + \text{CH}_4 \rightarrow \text{C}_2\text{H} + \text{CH}_3$	$5.05 \times 10^{-11} e^{-297/T}$	Pitts et al. (1982)
R37	$\text{C}_2\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_3$	$1.8 \times 10^{-11} e^{-302/T}$	from Lara et al. (1996)
R38	$\text{C}_4\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_4\text{H}_2 + \text{C}_2\text{H}_3$	1.4×10^{-10}	Vakhtin et al. (2001)
R39	${}^1\text{CH}_2 + \text{N}_2 \rightarrow {}^3\text{CH}_2 + \text{N}_2$	7.9×10^{-12}	Ashfold et al. (1981)
R40	${}^3\text{CH}_2 + {}^3\text{CH}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$	3.1×10^{-10}	Baulch et al. (1992)
R41	$\text{C}_2\text{H}_5 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_4$	$5.04 \times 10^{-14} T^{0.41} e^{429/T}$	Zhu et al. (2004)
R42	$\text{C}_2\text{H}_5 + \text{CH}_3 + \text{M} \rightarrow \text{C}_3\text{H}_8 + \text{M}$	$k_0 = 2.822 \times 10^{-3} T^{-8.749} e^{-985.4/T}$ $k_\infty = 2.41 \times 10^{-10} T^{-0.34} e^{-259/T}$	Lavvas et al. (2008) Zhu et al. (2004)
R43a	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_2$	2.81×10^{-12}	Tsang & Hampson (1986)
R43b	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_4$	2.81×10^{-12}	Tsang & Hampson (1986)
R44	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$	2.3×10^{-12}	Baulch et al. (1992)
R45	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 + \text{M} \rightarrow \text{C}_4\text{H}_{10} + \text{M}$	$k_0 = 6.723 \times 10^{-11} T^{-4.534}$ $k_\infty = 1.8 \times 10^{-11}$	Laufer et al. (1983); Baulch et al. (1992)
R46	$\text{C}_3\text{H}_3 + \text{H} + \text{M} \rightarrow \text{CH}_3\text{C}_2\text{H} + \text{M}$	$k_0 = 5.5 \times 10^{-27}$ $k_\infty = 2.5 \times 10^{-10}$	Moses et al. (2000) Homann & Wellmann (1983)

Table 1. continued.

	Reaction	Rate coefficient	Reference
R47a	$C_3H_5 + H \rightarrow CH_3C_2H + H_2$	1.5×10^{-11}	Hanning-Lee & Pilling (1992)
R47b	$C_3H_5 + H \rightarrow CH_2CCH_2 + H_2$	1.5×10^{-11}	Hanning-Lee & Pilling (1992)
R48a	$C_3H_5 + CH_3 \rightarrow CH_3C_2H + CH_4$	4.5×10^{-12}	Tsang (1991)
R48b	$C_3H_5 + CH_3 \rightarrow CH_2CCH_2 + CH_4$	4.5×10^{-12}	Tsang (1991)
R49	$C_3H_2 + H + M \rightarrow C_3H_3 + M$	$k_0 = 2.52 \times 10^{-28}$ $k_\infty = 5.0 \times 10^{-11}$	Moses et al. (2000)
R50	$^3CH_2 + C_2H_2 \rightarrow C_3H_3 + H$	$2.00 \times 10^{-11} e^{-3332/T}$	Tsang & Hampson (1986)
R51	$C_3H_8 + C_2H \rightarrow C_2H_2 + C_3H_7$	$9.8 \times 10^{-11} e^{-71/T}$	Murphy et al. (2003)
R52	$C_2H_3 + CH_3 + M \rightarrow C_3H_6 + M$	$k_0 = 6.0 \times 10^{-28} e^{1680/T}$ $k_\infty = 1.2 \times 10^{-10}$	Fahr et al. (1991)
R53	$C_3H_5 + H + M \rightarrow C_3H_6 + M$	$k_0 = 2.0 \times 10^{-28}$ $k_\infty = 1.0 \times 10^{-11}$	Moses et al. (2000) Hanning-Lee & Pilling (1992)
R54	$C_2H_3 + CH_3 \rightarrow C_2H_2 + CH_4$	3.4×10^{-11}	Fahr et al. (1991)
R55	$C_2H_3 + C_2H_5 + M \rightarrow C_4H_8 + M$	$k_0 = 2.822 \times 10^{-3} T^{-8.749} e^{-985.4/T}$ $k_\infty = 6.5 \times 10^{-11}$	Lavvas et al. (2008) Laufer & Fahr (2004)
R56	$C_3H_5 + CH_3 + M \rightarrow C_4H_8 + M$	$k_0 = 2.822 \times 10^{-3} T^{-8.749} e^{-985.4/T}$ $k_\infty = 1.55 \times 10^{-9} T^{-0.54} e^{117/T}$	Lavvas et al. (2008) Knyazev & Slagle (2001)
R57	$C_4H_2 + H + M \rightarrow C_4H_3 + M$	$k_0 = 1.0 \times 10^{-28}$ $k_\infty = 1.39 \times 10^{-10} e^{-1184/T}$	Schwanebeck & Warnatz (1975) Nava et al. (1986)
R58	$^*C_4H_2 \rightarrow C_4H_2 + hv$	1.0×10^3	Zwier & Allen (1996)
R59	$CH + C_2H_4 \rightarrow CH_3C_2H + H$	$3.87 \times 10^{-9} T^{-0.55} e^{-29.6/T}$	Canosa et al. (1997)

Table 2. Hörst et al. (2008) C-H-O reactions.

Reaction	Rate coefficient	Reference
R60	$O(^1S) \rightarrow O(^3D)$	Koyano et al. (1975)
R61	$O(^1D) \rightarrow O(^3P)$	Okabe (1978)
R62	$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	Sander et al. (2006)
R63	$O(^1D) + H_2 \rightarrow OH + H$	Sander et al. (2006)
R64a	$O(^1D) + CH_4 \rightarrow OH + CH_3$	Sander et al. (2006)
R64b	$O(^1D) + CH_4 \rightarrow CH_3O + H$	Sander et al. (2006)
R64c	$O(^1D) + CH_4 \rightarrow H_2CO + H_2$	Sander et al. (2006)
R65a	$O(^1D) + CO \rightarrow O(^3P) + CO$	Davidson et al. (1978)
R65b	$O(^1D) + CO \rightarrow CO_2$	Tully (1975)
	1.0×10^{-30}	Hörst et al. (2008)
R66a	$O(^3P) + CH_3 \rightarrow HCHO + H$	Hack et al. (2005)
R66b	$O(^3P) + CH_3 \rightarrow CO + H_2 + H$	Hack et al. (2005)
R67a	$O(^3P) + HCO \rightarrow CO_2 + H$	Baulch et al. (1992)
R67b	$O(^3P) + HCO \rightarrow CO + OH$	Baulch et al. (1992)
R68a	$O(^3P) + CH_3CO \rightarrow CO_2 + CH_3$	Baulch et al. (1992)
R68b	$O(^3P) + ^1CH_2 \rightarrow CH_2CO + OH$	Baulch et al. (1992)
R69	$OH + H_2 \rightarrow H_2O + H$	Atkinson et al. (2004)
R70	$OH + ^3CH_2 \rightarrow HCHO + H$	Tsang & Hampson (1986)
R71a	$OH + CH_3 \rightarrow H_2O + ^1CH_2$	Pereira et al. (1997)
	$6.4 \times 10^{-8} T^{5.8} e^{485/T}$	Pereira et al. (1997)
	$1.8 \times 10^{-8} T^{-0.91} e^{-275/T}$	Pereira et al. (1997)
R71b	$OH + CH_3 \rightarrow HCHO + H_2$	Pereira et al. (1997)
	$1.1 \times 10^{-17} T^{8.0} e^{1240/T}$	Pereira et al. (1997)
	$3.8 \times 10^{-14} T^{-0.12} e^{209/T}$	Pereira et al. (1997)
R71c	$OH + CH_3 \rightarrow CH_3OH$	Pereira et al. (1997)
	$7.2 \times 10^{-9} T^{-0.79}$	Pereira et al. (1997)
	$1.1 \times 10^{-10} T^{-6.21} e^{-671/T}$	Pereira et al. (1997)
R72	$OH + CH_4 \rightarrow H_2O + CH_3$	Atkinson et al. (2006)
R73	$OH + C_2H_2 \rightarrow CH_3CO$	Sander et al. (2006)
	$9.2 \times 10^{-18} T^2$	Sander et al. (2006)
	5.5×10^{-30}	Sander et al. (2006)
R74	$OH + C_2H_4 \rightarrow HOCH_2CH_2$	Sander et al. (2006)
	$1.1 \times 10^{-9} T^{-0.85}$	Sander et al. (2006)
	$1.4 \times 10^{-17} T^{-4.5}$	Sander et al. (2006)
R75a	$OH + CO \rightarrow CO_2 + H$	Atkinson et al. (2006)
R75b	$OH + CO \rightarrow HOCO$	Sander et al. (2006)
	$1.4 \times 10^{-13} (1 + [N_2]/4.2 \times 10^{19})$	Sander et al. (2006)
	$1.8 \times 10^{-9} T^{-1.3}$	Sander et al. (2006)
	$2.0 \times 10^{-36} T^{1.4}$	Sander et al. (2006)
R76	$HCO + H \rightarrow CO + H_2$	Baulch et al. (1992)
R77	$HCO + CH_3 \rightarrow CO + CH_4$	Tsang & Hampson (1986)
R78	$CH_3O + H \rightarrow HCHO + H_2$	Baulch et al. (1992)
R79	$CH_3O + CH_3 \rightarrow HCHO + CH_4$	Tsang & Hampson (1986)
R80a	$CH_3CO + CH_3 \rightarrow CO + C_6H_6$	Adachi et al. (1981)
R80b	$CH_3CO + CH_3 \rightarrow CH_2CO + CH_4$	Hassinen et al. (1990)
R80c	$CH_3CO + CH_3 \rightarrow CH_3COCH_3$	Hassinen et al. (1990)
	7.0×10^{-11}	Hörst et al. (2008)
	1.0×10^{-30}	Hörst et al. (2008)
R81	$C_2H + H_2O \rightarrow OH + C_2H_2$	Vanlook & Peeters (1995)
	$2.1 \times 10^{-12} e^{-200/T}$	

Table 3. Simplified set of C-H-O reactions derived from Dobrijevic et al. (2014, see text).

Reaction	Rate coefficient	Reference
R60	$2.15 \times 10^{-11} e^{110/T}$	Sander et al. (2011)
R61	1.1×10^{-10}	Sander et al. (2011)
R62a	1.05×10^{-10}	Atkinson et al. (2006)
R62b	3.5×10^{-11}	Atkinson et al. (2006)
R62c	7.5×10^{-12}	Atkinson et al. (2006)
R63a	1.1×10^{-10}	Baulch et al. (2005); Dobrijevic et al. (2014)
R63b	2.9×10^{-11}	Baulch et al. (2005); Dobrijevic et al. (2014)
R64a	1.0×10^{-11}	Böhland et al. (1984); Vinckier (1979); Shepler et al. (2007); Wang et al. (1973); Baulch et al. (2005); Zhang et al. (2004)
R64b	5.0×10^{-11}	Böhland et al. (1984); Vinckier (1979); Shepler et al. (2007); Wang et al. (1973); Baulch et al. (2005); Zhang et al. (2004)
R64c	6.0×10^{-11}	Böhland et al. (1984); Vinckier (1979); Shepler et al. (2007); Wang et al. (1973); Baulch et al. (2005); Zhang et al. (2004)
R65a	1.0×10^{-11}	Böhland et al. (1984); Vinckier (1979); Shepler et al. (2007); Wang et al. (1973); Baulch et al. (2005); Zhang et al. (2004)
R65b	5.0×10^{-11}	Böhland et al. (1984); Vinckier (1979); Shepler et al. (2007); Wang et al. (1973); Baulch et al. (2005); Zhang et al. (2004)
R65c	6.0×10^{-11}	Böhland et al. (1984); Vinckier (1979); Shepler et al. (2007); Wang et al. (1973); Baulch et al. (2005); Zhang et al. (2004)
R66a	$6.6 \times 10^{-12} e^{-1600/T}$	Baulch et al. (2005); Sander et al. (2011)
R66b	$2.6 \times 10^{-11} e^{-1600/T}$	Baulch et al. (2005); Sander et al. (2011)
R67a	$4.8 \times 10^{-13} (T/300)^{1.88} e^{-92/T}$	Baulch et al. (2005); Fu et al. (2012a,b); Balucani et al. (2012)
R67b	$5.0 \times 10^{-13} (T/300)^{1.88} e^{-92/T}$	Baulch et al. (2005); Fu et al. (2012a,b); Balucani et al. (2012)
R67c	$1.0 \times 10^{-13} (T/300)^{1.88} e^{-92/T}$	Baulch et al. (2005); Fu et al. (2012a,b); Balucani et al. (2012)
R67d	$3.0 \times 10^{-14} (T/300)^{1.88} e^{-92/T}$	Baulch et al. (2005); Fu et al. (2012a,b); Balucani et al. (2012)
R68a	6.0×10^{-11}	Heinemann et al. (1988); Harding et al. (2005); Dobrijevic et al. (2014)
R68b	1.0×10^{-11}	Heinemann et al. (1988); Harding et al. (2005); Dobrijevic et al. (2014)
R69a	5.0×10^{-11}	Harding et al. (2005); Hoyermann et al. (1999)
R69b	6.0×10^{-11}	Harding et al. (2005); Hoyermann et al. (1999)
R69c	3.0×10^{-11}	Harding et al. (2005); Hoyermann et al. (1999)
R70	$1.31 \times 10^{-11} e^{-678/T}$	Adamson et al. (1994)
R71	$2.8 \times 10^{-12} e^{-1800/T}$	Sander et al. (2011)
R72a	3.2×10^{-11}	De Avillez Pereira et al. (1997); Jasper et al. (2007); Sangwan et al. (2012)
R72b	8.0×10^{-12}	De Avillez Pereira et al. (1997); Jasper et al. (2007); Sangwan et al. (2012)
R72c	$k_0 = 2.0 \times 10^{-26} (T/300)^{-6} e^{-1000/T}$ $k_{\infty} = 1.2 \times 10^{-10} (T/300)^{-0.49}$	De Avillez Pereira et al. (1997); Jasper et al. (2007); Sangwan et al. (2012)
R73	$1.9 \times 10^{-12} e^{-1690/T}$	De Avillez Pereira et al. (1997); Jasper et al. (2007); Sangwan et al. (2012)
R74	$k_0 = 5.5 \times 10^{-30}$ $k_{\infty} = 8.3 \times 10^{-13} (T/300)^2$	Atkinson et al. (2006)
R75	$k_0 = 1.0 \times 10^{-28} (T/300)^{-4.5}$ $k_{\infty} = 7.5 \times 10^{-12} (T/300)^{-0.85}$	Sander et al. (2011)
R76	$1.68 \times 10^{-13} e^{-30/T} [1 + e^{-T/161} \frac{N_2}{7.88 \times 10^{18} T}]$	Sander et al. (2011)
R77	1.5×10^{-10}	Sander et al. (2011)
R78	9.3×10^{-11}	Sander et al. (2011)
R79a	3.0×10^{-12}	Sander et al. (2011)
R79b	3.0×10^{-11}	Atkinson et al. (2006)
		Baulch et al. (2005)
		Krasnoperov et al. (2005); Hébrard et al. (2013)
		Hoyermann et al. (1981); Dóbo et al. (1991)
		Hoyermann et al. (1981); Dóbo et al. (1991)

Table 3. continued.

Reaction	Rate coefficient	Reference
R80 $\text{CH}_3\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{CH}_4$	4.0×10^{-11}	Tsang & Hampson (1986)
R81 $\text{C}_2\text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{C}_2\text{H}_2$	$7.9 \times 10^{-24} (T/300)^{3.05} e^{-376/T}$	Carl et al. (2005)
R82 $\text{H} + \text{CO} \rightarrow \text{HCO}$	$k_0 = 7.5 \times 10^{-35} (T/300)^{0.2}$ $k_{\infty} = 1.2 \times 10^{-10} e^{-1000/T}$	Baulch et al. (2005) Wagner & Bowman (1987); Wang et al. (1973)
R83 $\text{H} + \text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{HCO}$	$3.3 \times 10^{-11} e^{-1850/T}$	Klemm (1979)
R84a $\text{H} + \text{CH}_3\text{CO} \rightarrow \text{CH}_3 + \text{HCO}$	4.0×10^{-11}	Bartels et al. (1991); Ohmori et al. (1990)
R84b $\text{H} + \text{CH}_3\text{CO} \rightarrow \text{H}_2\text{C}_2\text{O} + \text{H}_2$	2.0×10^{-11}	Bartels et al. (1991); Ohmori et al. (1990)
R85 $\text{CH} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO} + \text{H}$	$2.8 \times 10^{-11} (T/300)^{-1.22} e^{-12/T}$	Blitz et al. (1999); Bergeat et al. (2009); Hickson et al. (2013); Zabarnick et al. (1988)
R86 $\text{CH} + \text{H}_2\text{CO} \rightarrow \text{H}_2\text{C}_2\text{O} + \text{H}$	$1.0 \times 10^{-10} e^{-260/T}$	Zabarnick et al. (1988)
R87 $\text{CH} + \text{CO}_2 \rightarrow \text{H} + \text{CO} + \text{CO}$	$5.71 \times 10^{-12} e^{-345/T}$	Berman et al. (1982)
R88 $\text{CH}_3 + \text{CH}_3\text{O} \rightarrow \text{CH}_4 + \text{H}_2\text{CO}$	4.0×10^{-11}	Tsang & Hampson (1986)