Chemical pathway analysis of the Martian atmosphere: CO₂-formation pathways

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Abstract

The chemical composition of a planetary atmosphere plays an important role for atmospheric structure, stability, and evolution. Potentially complex interactions between chemical species do not often allow for an easy understanding of the underlying chemical mechanisms governing the atmospheric composition. In particular, trace species can affect the abundance of major species by acting in catalytic cycles. On Mars, such cycles even control the abundance of its main atmospheric constituent CO₂. The identification of catalytic cycles (or more generally chemical pathways) by hand is quite demanding. Hence, the application of computer algorithms is beneficial in order to analyze complex chemical reaction networks. Here, we have performed the first automated quantified chemical pathways analysis of the Martian atmosphere with respect to CO₂-production in a given reaction system. For this, we applied the Pathway Analysis Program (PAP) to output data from the Caltech/JPL photochemical Mars model. All dominant chemical pathways directly related to the global CO₂-production have been quantified as a function of height up to 86 km. We quantitatively show that CO₂-production is dominated by chemical pathways involving HOₓ and Oₓ. In addition, we find that NOₓ in combination with HOₓ and Oₓ exhibits a non-negligible contribution to CO₂-production, especially in Mars’ lower atmosphere. This study reveals that only a small number of chemical pathways contribute significantly to the atmospheric abundance of CO₂ on Mars; their contributions to CO₂-production vary considerably with altitude. This analysis also endorses the importance of transport processes in governing CO₂-stability in the Martian atmosphere. Lastly, we identify a previously unknown chemical pathway involving HOₓ, Oₓ, and HOₓ-photodissociation, contributing 8% towards global CO₂-production by chemical pathways using recommended up-to-date values for reaction rate coefficients.

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1. Introduction

One of the fundamental questions of planetary science concerns the photochemical stability of CO₂-dominated atmospheres in our Solar System, especially on Mars (95.32%, Owen et al., 1977). There, CO₂ is photolysed by solar UV radiation

\[
\text{CO}_2 + h\nu \rightarrow \text{CO} + \text{O},
\]

where atomic oxygen subsequently forms O₂. The termolecular formation reaction

\[
\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M}
\]

is not fast enough to compensate for the effective CO₂-destruction by photolysis. If one takes only the reaction products into account, one would therefore expect an atmosphere rich in CO and O₂, in contradiction to observations. This suggests that other mechanisms stabilize the observed CO₂ content of the Martian atmosphere. A first step in understanding the persistence of CO₂ in the Martian atmosphere was taken by McElroy and Donahue (1972) and Parkinson and Hunten (1972), who proposed chemical pathways involving Oₓ and HOₓ chemistry reproducing CO₂ from CO and O. These pathways can be understood as sets of chemical reactions, where molecules from the Oₓ-family (i.e. O and O₃) and the HOₓ-family (i.e. H, OH, and HO₂) or the HOₓ-family only, are acting as catalysts. This means that there is no net production or consumption of the catalyst species by the chemical pathways. Such chemical pathways can therefore provide efficient alternative routes for CO₂-production, even if the catalyst species are only present in trace amounts. Further improvements in photochemical models were made by the investigation of NOₓ (e.g., Krasnopolsky, 1993; Nair et al., 1994), and heterogeneous chemistry on dust and ice cloud particles (e.g.,

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Anbar et al., 1993; Atreya and Gu, 1994; Krasnopolsky, 1993; Lefèvre et al., 2008).

Several methods have been applied in order to gain more insight about chemical reaction systems in general. A variety of powerful methods use sensitivity analysis (for reviews, see Rabitz et al., 1983; Saltelli et al., 2005; Turányi, 1990), which aim at understanding the effects of uncertainties (e.g. in chemical reaction rate coefficients) on the chemical system. However, it is not possible to construct chemical pathways by sensitivity analysis methods only. The identification of chemical pathways is in general a demanding task and their manual construction is only possible for pathological examples or specific problems as e.g. methane photo-oxidation in Earth’s atmosphere (Johnston and Kinnison, 1998). Algorithms which take only stoichiometric information into account, were developed by e.g. Milner (1964), Clarke (1988), and Schuster and Schuster (1993). However, since these algorithms do not account for reaction rates (kinetic information), they cannot provide any quantitative information for individual chemical pathways. Therefore, using such methods it is not possible to determine, which chemical pathways dominate the reaction system. Moreover, these methods are usually not applicable to large reaction networks, because the number of pathways generally increases progressively with increasing number of reactions (“combinatorial explosion”).

The algorithm used in this study (PAP – Pathway Analysis Program) takes stoichiometric as well as kinetic information (i.e. reaction rates) into account and is capable of identifying and quantifying all significant chemical pathways for a given chemical reaction system. Developed by Lehmann (2004), it has been applied to Earth’s stratospheric ozone-chemistry (Lehmann, 2004; Saltelli et al., 2005) and Mars’ near surface atmospheric chemistry (Stock et al., 2011).

However, quantification of all dominant chemical pathways forming CO\textsubscript{2} in the whole Martian atmosphere is still lacking. In order to determine the contributions of individual chemical pathways to the altitude-dependent CO\textsubscript{2}-production, we apply the PAP algorithm to the results of the Caltech/JPL photochemical 1-D model of the Martian atmosphere. From this we derive the global mean CO\textsubscript{2}-production by each of these pathways.

2. Method

2.1. Pathway Analysis Program (PAP)

2.1.1. The algorithm

The Pathway Analysis Program (Lehmann, 2004) enables the identification and quantification of chemical pathways in arbitrary given reaction systems. For this purpose, starting with individual reactions as pathways, longer pathways are formed step by step by connecting shorter pathways at so-called ‘branching-point species’. At each step this branching-point species is chosen to be the species with the shortest lifetime with respect to the pathways formed in the previous steps. The algorithm terminates if a prescribed lifetime threshold \(\tau_{\text{max}}\) is reached or just before a prescribed species of interest \(S'\) would become a branching-point species.

When a chemical species \(S_i\) is treated as a branching-point species, then each pathway producing \(S_i\) is connected with each pathway consuming \(S_i\), in order to form a new longer pathway. A conservation of rates is valid, i.e. the sum of the rates of the new pathways “containing” a shorter pathway is equal to the rate of this shorter pathway. If the production and destruction rates of \(S_i\) are equal, the newly formed pathways recycle \(S_i\) completely, i.e. they are \(S_i\)-null-pathways. Otherwise, i.e. if there is a net concentration change of \(S_i\), a fraction of the rate of each pathway produc-

ing \(S_i\) (in the case of a net production of \(S_i\)) or consuming \(S_i\) (in the case of a net consumption of \(S_i\)) remains after the connection of pathways. These pathways and their (remaining) rates become a part of the final result of the pathway analysis, explaining the net production or consumption of \(S_i\).

Even if \(S_i\) has not been treated as a branching-point species, \(S_i\)-null-pathways may occur if the connection of pathways at a (shorter-lived) branching-point species \(S_j\) (\(i \neq j\)) forms pathways which recycle not only \(S_i\) (by construction), but also \(S_j\) (“coincidentally”).

In general, two problems can occur during the construction of chemical pathways when using a diagnostic algorithm. Firstly, the number of pathways can increase drastically with the number of reactions \(N_R\) and the number of species \(N_S\) due to “combinatorial explosion”. To deal with this problem, the PAP algorithm possesses the capability to identify insignificant pathways at an early stage of the analysis (Lehmann, 2004). Such pathways are rejected if their rates are smaller than a prescribed threshold rate \(f_{\text{min}}\). If \(f_{\text{min}}\) is chosen to be too large, potentially important pathways would be deleted and the total production or consumption of the species of interest can not be completely explained by the pathways determined using the algorithm. On the other hand, if \(f_{\text{min}}\) is chosen too small, required computational time and memory increase rapidly. The effect of the choice of the parameter \(f_{\text{min}}\) on the analysis results for Martian near-surface atmospheric conditions was discussed by Stock et al. (2011).

Secondly, chemical pathways can become unnecessarily complicated, e.g. containing null pathways as sub-pathways. In such cases the PAP algorithm splits the affected pathways into smaller (“elementary”) sub-pathways by the method described by Schuster and Schuster (1993) and Lehmann (2004). A more detailed description of the PAP algorithm can be found in Lehmann (2004). Further details related to the application on Martian chemistry are given by Stock et al. (2011).

2.1.2. Required input quantities

In order to determine chemical pathways, stoichiometric and kinetic data from the results of a photochemical model are needed by the PAP algorithm. These are

(i) a complete list of \(N_S\) chemical species and \(N_R\) reactions of the chemical system, where \(N_S \in \mathbb{N}\) and \(N_R \in \mathbb{N}\) are the total number of species and the total number of reactions, respectively,

(ii) the concentrations averaged over a time interval \([0, \Delta t]\)

\[
\langle n_i(x) \rangle := \frac{1}{\Delta t} \int_0^{\Delta t} n_i(x, t) \, dt, \quad i = 1, \ldots, N_S
\]

of all species, where \(n_i(x, t)\) is the concentration of species \(S_i\) at location \(x\) and time \(t\),

(iii) the time-averaged reaction rates

\[
\langle r_j(x) \rangle := \frac{1}{\Delta t} \int_0^{\Delta t} r_j(x, t) \, dt, \quad j = 1, \ldots, N_R
\]

of all reactions, where \(r_j(x, t)\) denotes the reaction rate of reaction \(R_j\) at location \(x\) and time \(t\), and

(iv) the concentration changes

\[
\Delta n_i(x) = \sum_{j=1}^{N_R} S_{ij} \langle r_j(x) \rangle \Delta t, \quad i = 1, \ldots, N_S
\]

caused by chemical reactions during the time interval \([0, \Delta t]\) for all species \(S_i\) located at \(x\), where \(S_{ij} \in \mathbb{R}\) are the components of the stoichiometric matrix.
2.2. Definitions

In this paper we will make use of the following definitions. In accordance with Lehmann (2004), we denote the stoichiometric coefficients of the net reaction of a pathway \( P_k \) with \( m_k \) \((m_k \in \mathbb{Z})\). These coefficients \( m_k \) are related to the stoichiometric coefficients \( s_{kj} \) of the individual reactions by

\[
m_k = \sum_{j=1}^{N_k} s_{kj} \delta_{jk}, \quad i = 1, \ldots, N_S, \quad k = 1, \ldots, N_P,
\]

where \( \delta_{jk} \in \mathbb{N} \cup \{0\} \) is the multiplicity of reaction \( R_j \) in pathway \( P_k \) and \( N_P \in \mathbb{N} \) the total number of chemical pathways. Additionally, we denote the mean rate of a pathway \( P_k \) in the time interval \([0, \Delta t]\) with \( f_k \). The rates of all reactions \( R_j \) are completely distributed to the chemical pathways \( P_k \), therefore the following relation holds:

\[
\langle r_j \rangle = \sum_{k=1}^{N_k} s_{kj}f_k, \quad j = 1, \ldots, N_S.
\]

Since all summands in Eq. (5) are non-negative, we obtain for each of them

\[
\delta_{jk}f_k \leq \langle r_j \rangle, \quad j = 1, \ldots, N_S, \quad k = 1, \ldots, N_P.
\]

If \( \delta_{jk} \neq 0 \), it follows:

\[
f_k \leq \frac{\langle r_j \rangle}{\delta_{jk}}; \quad j = 1, \ldots, N_S, \quad k = 1, \ldots, N_P.
\]

Consequently, the rate of pathway \( P_k \) cannot exceed

\[
f_{k}^{\max} = \min\left\{ \frac{\langle r_j \rangle}{\delta_{jk}} \mid \delta_{jk} \neq 0, \ j \in \{1, \ldots, N_k\} \right\}.
\]

The rate of the net change of species \( S_i \) by pathway \( P_k \) can be defined as

\[
\phi_{ik} := |m_k|f_k, \quad i = 1, \ldots, N_S, \quad k = 1, \ldots, N_P.
\]

From Eqs. (7) and (9) it immediately follows that

\[
\phi_{ik} \leq |m_k|\frac{\langle r_j \rangle}{\delta_{jk}}; \quad i = 1, \ldots, N_S, \quad k = 1, \ldots, N_P, \quad \forall j \in \{1, \ldots, N_k\} : \delta_{jk} \neq 0.
\]

This means that the rate of the net change of species \( S_i \) by pathway \( P_k \) is constrained by

\[
\rho_{ik} := \frac{|m_k|}{\delta_{jk}}\langle r_j \rangle,
\]

for each reaction \( R_j \) in pathway \( P_k \).

2.3. Photochemical column model

To obtain the required data to perform the pathway analysis of the Martian atmospheric chemistry, the reaction rate network equations

\[
\frac{\partial}{\partial t} n_i(x, t) + \text{div} \Phi_i(x, t) = P_i(n_1, \ldots, n_{N_S}) - L_i(n_1, \ldots, n_{N_S}),
\]

have to be solved, where \( P_i(n_1, \ldots, n_{N_S}) \) denotes the total production rate of species \( S_i \) by all chemical reactions and \( L_i(n_1, \ldots, n_{N_S}) \) the total loss rate by all chemical reactions, respectively. Here, we assume stationary conditions (i.e. \( \partial n_i/\partial t = 0 \)) and a plane-parallel geometry, where \( z \) denotes the altitude. The vertical flux of species \( S_i \) can then be described by

\[
\Phi_i = -D_i \left( \frac{\partial n_i}{\partial z} + \frac{n_i(1 + \chi_i)}{T} \frac{dT}{dz} \right) - K \left( \frac{\partial n_i}{\partial z} + \frac{n_i}{T} \frac{dT}{dz} \right),
\]

where \( D_i \) is the molecular diffusion coefficient, \( H \) the scale height, and \( \chi_i \) the thermal diffusion factor of species \( S_i \). \( K \) denotes the eddy diffusion coefficient and \( H \) the scale height of the background atmosphere.

We utilize the Caltech/JPL one-dimensional photochemical kinetics model for a latitude of 30° at equinox. This model is an update of the Nair et al. (1994) model. It is similar to that used by Yung et al. (1988) and Nair et al. (1994) to study the, overall, photochemical state of the Martian atmosphere. A detailed description of the 1-D photochemical model is given by Nair et al. (1994); we, therefore, only provide a short description of the model. Specifically, it incorporates Mars atmospheric oxygen, carbon, hydrogen, and nitrogen chemistry in the presence of vertical diffusive transport and allows for time-dependent calculations. It solves the 1-D continuity equation

\[
\frac{\partial}{\partial t} n_i(z, t) + \frac{\partial \Phi_i(z, t)}{\partial z} = \mathcal{P}_i(n_1, \ldots, n_{N_S}),
\]

for 27 species (O, O(1D), O2, O(1D), N2, N2O, NO, NO2, NO3, N2O5, HNO2, HNO3, HNO, H2O, H2O2, NO2, CO, CO2, O+, O2, H+, H2, H2O, OH, H2O2, CO, CO2, O, O2, CO2, and CO2+). The vertical flux is given by Eq. (13). The thermal diffusion factor \( \chi_i \) is set to be zero for all species \( S_i \) throughout our calculations.

2.4. Application: Martian atmosphere

For the chemical pathways analysis, the PAP algorithm is applied to the steady-state solution of the Caltech/JPL column model for each vertical layer separately. Due to the assumptions made, Eqs. (1) and (2) simply reduce to

\[
n_i(z) = n_i(z), \quad i = 1, \ldots, N_S
\]

and

\[
\langle r_j \rangle(z) = r_j(z), \quad j = 1, \ldots, N_S,
\]

respectively. The concentration changes \( \Delta n_i(z) \) caused solely by chemical reactions are obtained from Eq. (3). Although we have assumed steady-state, these concentrations changes \( \Delta n_i(z) \) are not necessarily zero, because of the divergence of the vertical flux \( \partial \Phi_i(z)/\partial z \) (see Eq. (14)). Since \( \Delta n_i(z) \) scales linearly with \( \Delta t \) for stationary conditions, the specific choice of the time-interval \( \Delta t \) does not affect the analysis results.

In order to determine the pathways responsible for the budget of the carbon-bearing species CO and CO2, we applied the PAP algorithm, such that the species of interest mentioned in Section 2.1.1 are CO and CO2. As described above, the choice of the branching-point species depends on their chemical lifetime. Since the chemical lifetime of a species \( S_i \) generally varies with altitude, it may happen that some species are considered as branching-point species only for a limited range of altitude. The threshold rate \( f_{\text{min}} \) (see Section 2.1.1) is chosen to be \( f_{\text{min}} = 10^{-9} \text{ppb h}^{-1} \) (see Stock et al. (2011) for discussion). With this choice, more than 99.983% of the total CO2-production by chemical pathways is identified by the PAP algorithm in each vertical layer.

The globally-averaged relative contribution to the production \( q_{ik} \) of a species \( S_i \) by a chemical pathway \( P_k \) is calculated by

\[
q_{ik} = \frac{\int_{0}^{\Delta t} \phi_{ik}(z) \, dz}{\int_{0}^{\Delta t} \sum_{i=1}^{N_S} \phi_{ik}(z) \, dz}, \quad \forall k \in \{1, \ldots, N_P\} : m_k > 0,
\]
where \( \varphi_{ai}(z) \) is defined in Eq. (9) and \( \Delta z \) is the extent of the atmosphere of interest. The value of \( \Delta z \) is set to 86 km for our analysis, because the major fraction of the global CO₂ production takes place below this level and proceeds via neutral chemistry (cf. Fig. 1). The error \( \epsilon_i \) caused by integrating only up to \( \Delta z = 86 \) km is estimated to be

\[
e_i = 1 - \frac{\int_0^{\Delta z} | \varphi_{ai}(z) | dz}{\int_0^{86 \text{ km}} | \varphi_{ai}(z) | dz},
\]

\( S_i \) = CO₂, where the upper boundary of the photochemical model is located at 240 km. The small value of \( \epsilon_i \) mainly results from the exponential decrease of the density with altitude. Note, that the scale height is \( H = 11.1 \) km at the Martian surface (Yung and DeMore, 1999). Thus, the choice of \( \Delta z = 86 \) km is sufficient for the purposes of this study.

3. Results and discussion

Fig. 1 shows the total CO₂-production and loss rate due to all chemical reactions. The production rate profile indicates, that there are two different chemical regimes in the Martian atmosphere. In the lower part of the atmosphere, i.e. \( z < 86 \) km, CO₂ is mainly formed from CO via

\[
\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}. \quad (R_{123})
\]

In the upper region of the atmosphere (\( z > 86 \) km) ionic chemistry becomes important. Here, CO₂ is mainly formed from CO₂ by charge-exchange ionization

\[
\text{CO}_2^+ + \text{O} \rightarrow \text{CO}_2 + \text{O}^+. \quad (R_{125})
\]

The destruction of CO₂ takes place mainly due to the photo-dissociation which yields CO via reaction R₂₇. Fig. 1 also illustrates that the modeled Martian atmosphere is not in kinetic equilibrium because the production rate \( P_{\text{CO}_2}(z) \) and loss rate \( L_{\text{CO}_2}(z) \) are not equal for each altitude. For higher altitudes (\( z > 43 \) km) CO₂ is effectively destroyed, whereas for lower altitudes (\( z < 43 \) km) CO₂ is effectively produced. Therefore, Fig. 2 shows a decrease in the volume mixing ratio of CO₂ and an increase in the volume mixing ratio of CO with altitude. This leads to an upward CO₂ flux accompanied by a downward CO flux due to (eddy-)diffusion (see Eq. (13)). The column integrated values of \( P_{\text{CO}_2}(z) \) and \( L_{\text{CO}_2}(z) \), however, are equal within the numerical uncertainty. Consequently, the Martian atmosphere is in this context chemically stable according to the model results. Since CO₂-production occurs mostly in the lower layers, we will focus our analysis on this part of the atmosphere.

The production rate of a species \( S_i \) by the sum of all chemical reactions which produce it (as in Fig. 1) is larger than or equal to the production rate by all \( S_i \) producing chemical pathways (Fig. 3), because a fraction of the \( S_i \) producing reaction rate may be distributed to \( S_i \)-null-pathways (cf. Section 2.1.1). An example of a CO₂-null-pathway is pathway \( P_{14} \). In the following, the term CO₂-production corresponds to the CO₂-production by CO₂-non-null-pathways. In order to discuss the CO₂-production-pathways found by the PAP algorithm, it is convenient to group certain species into chemical families termed: HOₓ (\( =\text{H} + \text{OH} + \text{HO}_2 \)), Oₓ (\( =\text{O} + \text{O}_3 \)), and NOₓ = NO + NO₂). This convention results in three classes of dominant pathways in our chemical reaction system, which can be further divided into smaller (sub-)groups according to specific reactions (see Table 1). In Fig. 3 the contributions of the most efficient pathways are shown. Each of the nine dominant pathways has at least 3% contribution to the total CO₂-production by chemical pathways in one or more layers up to \( z \leq 86 \) km. The dominant pathways, presented in this study, account for 96.6% of CO₂-production. The remaining 3.4% are due to a large number of chemical pathways that individually contribute a minor fraction to the CO₂-production. This is due to an increasing mixing ratio of NOₓ in the lower part of the atmosphere, which leads to higher reaction rates of NOₓ-involving reactions and therefore a larger efficiency of \( \text{O}_x \text{-HO}_x \text{-NO}_x \)-pathways.

3.1. Class I: \( \text{O}_x \text{-HO}_x \)-pathways

The \( \text{O}_x \text{-HO}_x \)-pathways in Tables 2 and 3 (\( P_1 \text{–} P_6 \)) found in this study can be further split into two sub-groups, depending on

![Fig. 1. CO₂-production rates. Total CO₂-production rate \( P_{\text{CO}_2}(z) \) (solid line) and total destruction rate \( L_{\text{CO}_2}(z) \) (dotted line) by all chemical reactions. Dashed curves indicate the rates of the reactions with the largest contributions to the total CO₂-production.](image)

![Fig. 2. Modeled CO and CO₂ volume mixing ratio altitude profiles. \( n_{\text{tot}} \) denotes the total number density of the atmosphere at given altitude.](image)

<table>
<thead>
<tr>
<th>Class</th>
<th>Ia</th>
<th>Ib</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_x )</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>( \text{HO}_x )</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>( \text{NO}_x )</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Pathway</td>
<td>( P_1 )</td>
<td>( P_2 )</td>
<td>( P_3 )</td>
<td>( P_4 )</td>
</tr>
<tr>
<td>( \text{O}_x \text{-HO}_x \text{-NO}_x )-pathways</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

Table 1 Classification of CO₂-production-pathways in this paper. The first row lists the nine dominant CO₂-production-pathways. In the first column the families are shown. A bullet (•) indicates that a molecule from the family is participating in the given pathway. The last row denotes the pathway class.
Table 2
Class la O$_2$-HO$_x$-pathway percentage-contribution to the global CO$_2$-production by all CO$_2$-production-pathways. Values on the right hand side are calculated according to Eq. (17).

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Reaction</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>P$_1$</td>
<td>O$_2$ + hv $\rightarrow$ O + O&lt;br&gt;2 (O + HO$_2$ $\rightarrow$ OH + O$_2$)&lt;br&gt;2 (CO + OH $\rightarrow$ CO$_2$ + H)&lt;br&gt;2 (H + O$_2$ + M $\rightarrow$ HO$_2$ + M)</td>
<td>net: 2CO + O$_2$ $\rightarrow$ 2CO$_2$ 40.2%</td>
</tr>
<tr>
<td>P$_2$</td>
<td>O + HO$_2$ $\rightarrow$ OH + O$_2$&lt;br&gt;CO + OH $\rightarrow$ CO$_2$ + H&lt;br&gt;H + O$_2$ + M $\rightarrow$ HO$_2$ + M</td>
<td>net: CO + O $\rightarrow$ CO$_2$ 18.5%</td>
</tr>
<tr>
<td>P$_3$</td>
<td>HO$_2$ + hv $\rightarrow$ OH + O&lt;br&gt;2 (CO + OH $\rightarrow$ CO$_2$ + H)&lt;br&gt;2 (H + O$_2$ + M $\rightarrow$ HO$_2$ + M)</td>
<td>net: 2CO + O$_2$ $\rightarrow$ 2CO$_2$ 7.9%</td>
</tr>
<tr>
<td>P$_4$</td>
<td>O$_2$ + hv $\rightarrow$ O + O&lt;br&gt;O + HO$_2$ $\rightarrow$ OH + O$_2$&lt;br&gt;CO + OH $\rightarrow$ CO$_2$ + H&lt;br&gt;H + O$_2$ + M $\rightarrow$ HO$_2$ + M</td>
<td>net: CO + O$_2$ $\rightarrow$ CO$_2$ 6.3%</td>
</tr>
</tbody>
</table>

Table 3
Class lb O$_2$-HO$_x$-pathway percentage-contribution to the global CO$_2$-production by all CO$_2$-production-pathways. Values on the right hand side hand side are calculated according to Eq. (17).

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Reaction</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>P$_5$</td>
<td>O + O$_2$ + CO$_2$ $\rightarrow$ O$_3$ + CO$_2$&lt;br&gt;H + O$_2$ $\rightarrow$ OH + O$_2$&lt;br&gt;CO + OH $\rightarrow$ CO$_2$ + H</td>
<td>net: CO + O $\rightarrow$ CO$_2$ 6.3%</td>
</tr>
<tr>
<td>P$_6$</td>
<td>O$_2$ + hv $\rightarrow$ O + O&lt;br&gt;2 (O + O$_2$ + CO$_2$ $\rightarrow$ O$_3$ + CO$_2$)&lt;br&gt;2 (H + O$_2$ + O$_2$ $\rightarrow$ HO$_2$ + O$_2$)&lt;br&gt;2 (CO + OH $\rightarrow$ CO$_2$ + H)</td>
<td>net: 2CO + O$_2$ $\rightarrow$ 2CO$_2$ 1.6%</td>
</tr>
</tbody>
</table>

Fig. 3. Rate of the net change of CO$_2$ via CO$_2$-production-pathways. Solid lines indicate the contribution of the nine dominant pathways. The dotted line represents the total production of CO$_2$ by all CO$_2$-production-pathways. The dashed line is the sum of the contribution of the nine dominant pathways.

how H is transformed into OH. This proceeds either via the reaction with O$_2$ (sub-class la)<br>H + O$_2$ + M $\rightarrow$ HO$_2$ + M, ($R_{47}$)<br>O + HO$_2$ $\rightarrow$ OH + O$_2$, ($R_{47}$)

or via reaction with O$_3$ (sub-class lb)<br>H + O$_3$ $\rightarrow$ OH + O$_2$, ($R_{52}$)

3.1.1. Class la

Three of the pathways shown in Table 2 (P$_1$, P$_2$, P$_4$) are variations of the chemical scheme presented by McElroy and Donahue (1972). Since atomic oxygen has a short chemical lifetime in the lower part of the atmosphere relevant for CO$_2$-production, the PAP algorithm identifies it as a branching-point species. The atomic oxygen originates chemically mostly from either photolysis of molecular oxygen (P$_1$) or photolysis of ozone (P$_2$). Alternatively, atomic oxygen can be supplied by vertical transport due to eddy-diffusion (P$_4$). There is also the possibility to provide atomic oxygen via the photo-dissociation of CO$_2$ (reaction $R_{27}$). However, this will result in null pathways, which are neither producing nor consuming CO$_2$.

The rates of the production pathways $f_k(z)$ are naturally bounded from above by $f_{max}(z)$ (see Section 2.2). However, in several cases this bound is not reached over wide altitude ranges as a result of competition with other chemical pathways (see Fig. 4a or Fig. 6b for example). In the following, we will therefore investigate the competing pathways in order to elucidate the interactions within the reaction network, when necessary.

Fig. 4a suggests that pathway P$_1$ is most efficient at $z = 4$ km and has the largest contribution to the global CO$_2$-production of all pathways identified in this study. Above $z = 4$ km its rate decreases monotonically with altitude. This is mainly due to the decrease of the atomic oxygen concentration with increasing altitude. However, not all atomic oxygen produced by reaction P$_1$ is consumed by P$_1$ (Fig. 4a). In order to investigate the fate of atomic oxygen produced by reaction P$_1$ between $z = 0$ km and $z = 12$ km (lower regime) as well as $z = 34$ km and $z = 51$ km (upper regime), we use PAP to find all pathways which include reaction P$_1$.

In the lower regime atomic oxygen produced by O$_2$-photolysis (reaction $R_1$) and not consumed by P$_1$ is primarily used for CO$_2$-production by pathways such as P$_5$ or the following:

O$_2$ + hv $\rightarrow$ O + O<br>2 (O + NO$_2$ $\rightarrow$ NO + O$_2$)<br>2 (HO$_2$ + NO $\rightarrow$ NO$_2$ + OH)<br>2 (CO + OH $\rightarrow$ CO$_2$ + H)<br>2 (H + O$_2$ + M $\rightarrow$ HO$_2$ + M) (P$_10$

The pathways with the largest rates found by this search in the upper regime (Fig. 4a) are beside P$_1$ the null pathways O$_2$ + hv $\rightarrow$ O + O<br>O + HO$_2$ $\rightarrow$ OH + O$_2$<br>O + OH $\rightarrow$ O$_2$ + H<br>H + O$_2$ + M $\rightarrow$ HO$_2$ + M

and

O$_2$ + hv $\rightarrow$ O + O<br>O + OH $\rightarrow$ O$_2$ + H<br>O + O$_2$ + CO$_2$ $\rightarrow$ O$_3$ + CO$_2$

H + O$_3$ $\rightarrow$ OH + O$_2$, (P$_{11}$)

O + HO$_2$ $\rightarrow$ OH + O$_2$, (P$_{12}$)
Since above $z = 51$ km the rate of $P_i$ cannot exceed the half of the reaction rate of the CO$_2$-forming reaction $R_{123}$, which also determines $f_{\text{max}}(z)$ in this region, one might also be interested in the fate of atomic hydrogen produced by reaction $R_{123}$. Only a small fraction of atomic hydrogen is here recycled by CO$_2$-production-pathways $P_5$ and $P_6$, or by the null pathways.

$$
\begin{align*}
\text{CO}_2 + h\nu & \rightarrow \text{CO} + O \\
\text{O} + \text{O}_2 + \text{CO}_2 & \rightarrow \text{O}_3 + \text{CO}_2 \\
\text{H} + \text{O}_3 & \rightarrow \text{OH} + \text{O}_2 \\
\text{CO} + \text{OH} & \rightarrow \text{CO}_2 + \text{H}
\end{align*}
$$

with net reactions:

$$
\begin{align*}
\text{net} & : \text{null, (P13)} \\
\text{net} & : \text{null. (P14)}
\end{align*}
$$

At altitudes $34 \text{ km} < z < 48 \text{ km}$ CO$_2$-production is dominated by pathway $P_2$ (Fig. 3). In this part of the atmosphere, atomic oxygen is supplied by downward transport. Eq. (8) can be modified by treating transport processes of species $S_i$ with $\tau_i < \tau_{\text{max}}$ or $\tau_i < \tau_{\text{s}}$ as pseudo reactions, where $\tau_{\text{s}}$ is the lifetime of $S'$.}

Since above $z = 51$ km the rate of $P_i$ cannot exceed the half of the reaction rate of the CO$_2$-forming reaction $R_{123}$, which also determines $f_{\text{max}}(z)$ in this region, one might also be interested in the fate of atomic hydrogen produced by reaction $R_{123}$. Only a small fraction of atomic hydrogen is here recycled by CO$_2$-production-pathways $P_5$ and $P_6$, or by the null pathways.

$$
\begin{align*}
\text{CO}_2 + h\nu & \rightarrow \text{CO} + O \\
\text{O} + \text{O}_2 + \text{CO}_2 & \rightarrow \text{O}_3 + \text{CO}_2 \\
\text{H} + \text{O}_3 & \rightarrow \text{OH} + \text{O}_2 \\
\text{CO} + \text{OH} & \rightarrow \text{CO}_2 + \text{H}
\end{align*}
$$

with net reactions:

$$
\begin{align*}
\text{net} & : \text{null, (P13)} \\
\text{net} & : \text{null. (P14)}
\end{align*}
$$

At altitudes $34 \text{ km} < z < 48 \text{ km}$ CO$_2$-production is dominated by pathway $P_2$ (Fig. 3). In this part of the atmosphere, atomic oxygen is supplied by downward transport. Eq. (8) can be modified by treating transport processes of species $S_i$ with $\tau_i < \tau_{\text{max}}$ or $\tau_i < \tau_{\text{s}}$ as pseudo reactions, where $\tau_{\text{s}}$ is the lifetime of $S'$. (cf. Section 2.1.1). Therefore the oxygen flux divergence is an upper bound to the rate of $P_2$ up to $z = 40$ km (Fig. 4b). The atomic oxygen, which is vertically transported and not consumed by pathway $P_2$ forms O$_2$ via

$$
\begin{align*}
\text{O} + \text{HO}_2 & \rightarrow \text{OH} + \text{O}_2 \\
\text{O} + \text{OH} & \rightarrow \text{O}_2 + \text{H} \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M}
\end{align*}
$$

with net:

$$
\begin{align*}
\text{net} & : 2\text{O} \rightarrow \text{O}_2, \quad (P_{15})
\end{align*}
$$

or CO$_2$ by pathway $P_6$. Above this altitude range, $f_{\text{max}}(z)$ is determined by the CO$_2$-formation reaction $R_{123}$. The atomic hydrogen produced by this reaction and not consumed by pathway $P_2$ is used by the CO$_2$-production-pathway $P_4$ and the null pathway $P_{16}$.

Here, we present for the first time a newly identified chemical CO$_2$-production-pathway – i.e. $P_3$ (see Table 2 and Fig. 4c), which accounts for ~8% of the total CO$_2$-production. It is characterized by HO$_2$ photolysis

$$
\begin{align*}
\text{HO}_2 + h\nu & \rightarrow \text{OH} + \text{O}.
\end{align*}
$$

The rate of reaction $R_8$ has a maximum around $z = 12$ km, a result of two competing processes (Fig. 4c). Above $z = 8$ km, the HO$_2$ concentration decreases with increasing altitude (Fig. 5a), whereas below $z = 24$ km, the rate coefficient of reaction $R_8$ increases with increasing altitude due to absorption and scattering of the incoming UV-radiation. A minor contribution to the global CO$_2$-production is
made by pathway $P_5$. This pathway is completely limited by the
supply of ozone due to vertical transport (Fig. 4d). Its rate has
two distinct clear cut maxima at $z = 6$ km and $z = 36$ km. The upper
maximum depends on the downward transport of ozone from
upper layers. The lower maximum originates from the upward
transport of ozone from the lower layers (Fig. 5b).

3.1.2. Class Ib

The remaining two O$_3$-HO$_x$-pathways, $P_5$ and $P_6$ (Table 3), are
variations of scheme Ib presented by Yung and DeMore (1999).
For pathway $P_5$, atomic oxygen is supplied by downward transport
from the upper atmosphere. However, in this case, the oxygen
transport is not the limiting factor, since in the part of the atmo-
sphere where pathway $P_5$ has its maximum rate, sufficient atomic
oxygen is provided by the O$_2$-photolysis reaction (Fig. 6a). For altitudes between
$z = 30$ km and $z = 45$ km, the rate of pathway $P_5$ is bounded from
above by the O$_2$-formation reaction $R_{52}$. The majority of OH pro-
duced by reaction $R_{52}$ and not consumed by pathway $P_5$ is either
trapped in the null pathway $P_{13}$ or used for O$_2$-production via

\[
\begin{align*}
O + OH &\rightarrow O_2 + H \\
H + O_3 &\rightarrow OH + O_2 \\
O + O_3 + CO_2 &\rightarrow O_3 + CO_2
\end{align*}
\]

net : 20 $\rightarrow$ O$_2$. 

The difference between pathways $P_5$ and $P_6$ is the source of
atomic oxygen. While the atomic oxygen in pathway $P_5$ comes
from the upper atmosphere by transport, in case of pathway $P_6$
the atomic oxygen is produced by the O$_2$-photolysis reaction $R_1$
(Table 3). There are three regions, where $f_{\text{max}}(z)$ is determined by
three different reactions (Fig. 6b). Below $z = 34$ km it is reaction

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Pathway & Contribution to Global CO$_2$-Production \%
\hline
$P_5$ & 8.2 \%
$P_6$ & 1.4 \%
\hline
\end{tabular}
\caption{Class II HO$_x$-pathway percentage-contribution to the global CO$_2$-production by all CO$_2$-production-pathways. Values on the right hand side are calculated according to Eq. (17).}
\end{table}

At higher altitudes, i.e. $z \geq 45$ km, the reaction with the smallest
rate occurring in pathway $P_5$ is the CO$_2$-formation reaction $R_{123}$.
Atomic hydrogen produced by this reaction is mainly involved in
CO$_2$-production by pathways $P_2$ and $P_5$.

The difference between pathways $P_5$ and $P_6$ is the source of
atomic oxygen. While the atomic oxygen in pathway $P_5$ comes
from the upper atmosphere by transport, in case of pathway $P_6$
the atomic oxygen is produced by the O$_2$-photolysis reaction $R_1$
(Table 3). There are three regions, where $f_{\text{max}}(z)$ is determined by
three different reactions (Fig. 6b). Below $z = 34$ km it is reaction

\begin{align*}
R_{123}: CO + OH &\rightarrow CO_2 + H \\
R_{45}: O + O_3 + CO_2 &\rightarrow O_3 + CO_2
\end{align*}
than its potential maximum rate produced by reaction R123. In the lower regime, OH produced by reaction R7 was previously introduced by Parkinson and Hun-ten (1972). The rate of pathway P7 is restricted by reactions R12 and R72

\[
\text{The reaction rate of } \text{HO}_2 + \text{H} \xrightarrow{R12} \text{H}_2\text{O}_2 + \text{OH}.
\]

The pathway P7 was previously introduced by Parkinson and Hun-ten (1972). The rate of pathway P7 is restricted by reactions R12 and R72

\[\text{where the latter produces } \text{H}_2\text{O}_2, \text{which is subsequently photolyzed via reaction } R12 (\text{Fig. 7a}). \text{Pathway } P_8 \text{, proposed by Sonnemann et al. (2006), has only a minor contribution to the global } \text{CO}_2\text{-production. Its rate } f_{\text{R8}}(z) \text{ is basically limited by the reaction}
\]

\[
\text{H + } \text{HO}_2 \rightarrow \text{OH} + \text{OH}. \quad (\text{R8})
\]

The reaction rate of R8 is characterized by an increase of the concentration of H and a decrease of the concentration of HO2 with altitude (Figs. 5a and 7b).

3.3. Class III: \(\text{O}_x-\text{HO}_x-\text{NO}_x\)-pathways

The third class of dominant chemical pathways in this study contains only one pathway, namely P8 (see Table 5), which includes additional species from the NOx-family as catalysts. This pathway is especially important at altitudes below \(z = 30 \text{ km}\) (Fig. 8). There, \(f_{\text{R8}}(z)\) is determined by the rate \(f_{\text{R17}}(z)\) of NO2-photolysis

\[
\text{NO}_2 + \text{h} \nu \rightarrow \text{NO} + \text{O}. \quad (\text{R17})
\]

Below \(z = 12 \text{ km}\) NO and O, which are produced by this reaction and not consumed by P8 are mainly trapped in the null pathways

\[
\begin{align*}
\text{NO}_2 + \text{h} \nu & \rightarrow \text{NO} + \text{O}, \\
\text{O}_1 + \text{NO} & \rightarrow \text{NO}_2 + \text{O}_2, \\
\text{O} + \text{O}_2 + \text{CO}_2 & \rightarrow \text{O}_3 + \text{CO}_2, \\
\text{net: } & \text{null}. \quad (\text{P18})
\end{align*}
\]

and

\[
\begin{align*}
\text{NO}_2 + \text{h} \nu & \rightarrow \text{NO} + \text{O}, \\
\text{O} + \text{NO} + \text{M} & \rightarrow \text{NO}_2 + \text{M}, \\
\text{net: } & \text{null}. \quad (\text{P19})
\end{align*}
\]

3.4. Global contribution of \(\text{CO}_2\)-production-pathways

The global relative contribution of the individual \(\text{CO}_2\)-production-pathways to the total \(\text{CO}_2\)-production by chemical pathways.

\[\text{Table 5}
\]
pathways which require O. Individual pathways belong. The black circular ring segment indicates chemical pathways which account for more than 96% of the CO₂-production. 

atmosphere (see Fig. 3), where NO

photochemical absorption cross-sections, reaction rate coefficients, 

tian atmosphere. 

Contribution of chemical pathways to the global CO₂-production calculated in the literature, are marked “new”. The outer ring points to which class the individual pathways belong. The black circular ring segment indicates chemical pathways which require O₂ by vertical transport. Pathways, previously not reported in the literature, are marked “new”.

Fig. 8. Altitude-dependence of rates associated with pathway Pₙ. The solid line indicates the rate of CO₂-production by pathway Pₙ (qₙ from Eq. (9) with Sₙ = CO₂, Pₙ = Pₙ). Dashed lines show the constraints on the rate of CO₂-production by pathway Pₙ imposed by individual reactions (ρₙ from Eq. (11) with Sₙ = CO₂, Pₙ = Pₙ). Note that ρₙ with Rₙ = Rₙ and ρₙ with Rₙ = Rₙ do not lie on top of each other, since Rₙ occurs twice in pathway Pₙ, but Rₙ only once.

Fig. 9. Contribution of chemical pathways to the global CO₂-production calculated according to Eq. (17). The inner circular disk shows the relative contributions of the individual pathways to the global CO₂-production. Numerical values are given in the corresponding Tables 2 and 5. The outer ring points to which class the individual pathways belong. The black circular ring segment indicates chemical pathways which require O₂ by vertical transport. Pathways, previously not reported in the literature, are marked “new”.

qₙ is calculated using Eq. (17). Fig. 9 shows the nine dominant pathways which account for more than 96% of the CO₂-production. The largest contribution is thereby made by O₃–HO₃ pathways (76.6%), followed by the O₃–HO₂–NO pathways (10.4%), and O₃–HO₂ pathways (9.6%). The remaining 3.4% are produced by summing a large number of pathways, which have only a minor contribution. These pathways occur especially in the lower layers of the atmosphere (see Fig. 3), where NO₂-chemistry becomes more important. Pathways which depend on the vertical transport of either atomic oxygen or ozone have a contribution of 26.9%. This suggests that transport processes have a significant impact on CO₂-production and hence the photochemical stability of the Martian atmosphere.

3.5. Uncertainties

All input parameters required by photochemical models (e.g. photochemical absorption cross-sections, reaction rate coefficients, eddy-diffusion profiles, etc.) are clearly only known within a certain range of uncertainty. These uncertainties can affect the time-averaged concentrations (nᵢ)(z) of chemical species as well as the time-averaged chemical reaction rates (rᵢ)(z) which in turn can influence the results of the pathway analysis. The same is also true for numerical uncertainties. However, numerical errors are negligible in comparison to the uncertainties in the input parameters.

To investigate the effect of the above uncertainties on the results of the pathway analysis, a comprehensive global sensitivity analysis would be required in order to account for the non-linear behavior of the modeled atmosphere. Such an analysis would require a large number of simulations to obtain statistically relevant results and highly sophisticated numerical techniques to identify the key-uncertainties (Dobrijevic et al., 2010) and is therefore beyond the scope of this paper.

Nevertheless, the identification of the dominant pathways can give an indication of those chemical reactions, which have a significant influence on the CO₂ abundance as calculated by the Caltech/JPL photochemical column model. Out of 126 reactions, only 13 participate in the nine dominant CO₂-production-pathways P₁–P₉ (see A1). Whereas sensitivity analysis methods can pinpoint key-reactions which strongly impact the numerical solutions of photochemical models, PAP provides information regarding the interrelationship between chemical reactions. The pathway analysis of chemical reaction networks can therefore be regarded as complementary to standard sensitivity analysis methods. Combined pathway and sensitivity analyses will be the subject of future studies.

3.6. Impact of potentially missing trace species and reactions

The PAP algorithm identifies all significant pathways in a given reaction system. Trace gas species or reactions not included can therefore not be detected by this algorithm.

For example, a species which is present on Mars, but not part of the reaction scheme is ⁴⁰Ar (Owen et al., 1977). Being a noble-gas, ⁴⁰Ar is chemically inactive and does not take part in chemical gas-phase reactions. Therefore, the outcome of the pathway analysis will not be affected by neglecting ⁴⁰Ar in the chemical scheme.

More interesting effects are expected by adding more reactive species, like the activated complex HOCO⁺ to the reaction network. HOCO⁺ can be formed via CO + OH → HOCO⁺ (R₁₂₃a)

and can react further to HOCO⁺ → CO₂ + H (R₁₂₃b) (Smith and Zellner, 1973; Senosiain et al., 2003), replacing reaction R₁₂₃. If HOCO⁺ decomposes into the products given by reaction R₁₂₃b before it can react with other species, no significant changes, except the separation of reaction R₁₂₃ into two parts (reactions R₁₂₃a and R₁₂₃b), will be seen in the identified pathways. Significant changes might occur if HOCO⁺ can be thermally stabilized

HOCO⁺ + M → HOCO + M. (R₁₂₃c)

In this case the probability for HOCO taking part in bimolecular reactions becomes more probable, forming potentially new pathways (Boxe et al., 2010). The role for the Martian atmospheric chemistry of potentially missing species and reactions can be investigated by expanding the current scheme used in the Caltech/JPL photochemical column model presuming reaction rate coefficients are known or can be estimated. The PAP-algorithm can then be used again to assess the relevance of newly added species and reactions in relation to the existing well-established reaction network.
4. Summary and conclusions

In order to address the CO₂ stability problem of the Martian atmosphere, we have applied for the first time the Pathway Analysis Program (PAP) to the modified Caltech/JPL photochemical column model of the Martian atmosphere. All dominant CO₂-production-pathways in the underlying reaction network throughout the lower to middle atmosphere, where CO₂-production is efficient, have been identified and quantified. Our results are in good agreement with previous studies (e.g. McElroy and Donahue, 1972; Parkinson and Hunten, 1972; Yung and DeMore, 1999) which proposed the most dominant pathways involving HO₃ and NO₃ respectively. The algorithm was also capable to identify pathways with minor contributions, e.g. \( P_{3} \) (Sonnemann et al., 2006). In addition, we have calculated relative contributions of chemical pathways to the global CO₂-production in Mars’ atmosphere. We have calculated pathway rates as functions of altitude, whereby the efficiency of individual pathways varies drastically with altitude. Furthermore, our investigations revealed that in some cases a significant discrepancy between the actual rate of a pathway \( f_{i}(z) \) and its potential maximum rate \( f_{\text{max}}(z) \) can occur. This phenomenon is a consequence of the competition between pathways, which also has been determined in this study. Almost 27% of CO₂-production is due to chemical pathways, which consume the species O or O₃. These have a relatively short lifetime in comparison to the time-scale of CO–CO₂-interconversion and are provided by vertical transport. This in turn indicates a close coupling between dynamical and chemical processes in the Martian atmosphere. The study is the first to quantify the contribution of specific chemical pathways towards the overall stability of the atmosphere. Therefore results herein provide deeper insights towards the role of trace gases being measured by future missions like, e.g. the ExoMars Trace Gas Orbiter (Wittase and Allen, 2011).

Acknowledgment

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Appendix A. Chemical reactions in the Caltech/JPL Mars atmosphere model

See Table A1.

Table A1

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_1 )</td>
<td>( O_3 + h_v \rightarrow O + O )</td>
</tr>
<tr>
<td>( R_2 )</td>
<td>( O_3 + h_v \rightarrow O + O(D) )</td>
</tr>
<tr>
<td>( R_3 )</td>
<td>( O_3 + h_v \rightarrow O + O )</td>
</tr>
<tr>
<td>( R_4 )</td>
<td>( O_3 + h_v \rightarrow O + O(\Delta) )</td>
</tr>
<tr>
<td>( R_5 )</td>
<td>( O_3 + h_v \rightarrow O + O )</td>
</tr>
<tr>
<td>( R_6 )</td>
<td>( H_2 + O + H )</td>
</tr>
<tr>
<td>( R_7 )</td>
<td>( OH + h_v \rightarrow O + H )</td>
</tr>
<tr>
<td>( R_8 )</td>
<td>( HO_2 + h_v \rightarrow OH + O )</td>
</tr>
<tr>
<td>( R_9 )</td>
<td>( H_2O + h_v \rightarrow H + OH )</td>
</tr>
<tr>
<td>( R_{10} )</td>
<td>( H_2O + h_v \rightarrow H + O_2 )</td>
</tr>
<tr>
<td>( R_{11} )</td>
<td>( H_2O + h_v \rightarrow H + H + O )</td>
</tr>
<tr>
<td>( R_{12} )</td>
<td>( HO_2 + h_v \rightarrow OH + OH )</td>
</tr>
<tr>
<td>( R_{13} )</td>
<td>( N_2 + h_v \rightarrow N + N )</td>
</tr>
<tr>
<td>( R_{14} )</td>
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</tr>
<tr>
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<td>( R_{26} )</td>
<td>( HNO_3 + h_v \rightarrow NO + HO )</td>
</tr>
<tr>
<td>( R_{27} )</td>
<td>( CO_2 + h_v \rightarrow CO + O )</td>
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<td>( R_{28} )</td>
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<tr>
<td>( R_{29} )</td>
<td>( O + M \rightarrow O^+ + e^- + M )</td>
</tr>
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</tr>
<tr>
<td>( R_{31} )</td>
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<td>( R_{33} )</td>
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</tr>
<tr>
<td>Reaction</td>
<td>Rate coefficient</td>
</tr>
<tr>
<td>----------</td>
<td>------------------</td>
</tr>
<tr>
<td>R44: ( R_4^+ + e^- \rightarrow CO + O )</td>
<td>( 3.8 \times 10^{-7} )</td>
</tr>
<tr>
<td>R45: ( CO_2^+ + e^- \rightarrow CO_2 + H )</td>
<td>( 3.0 \times 10^{-7} )</td>
</tr>
<tr>
<td>R46: ( O^+ \rightarrow CO + O )</td>
<td>( 9.6 \times 10^{-10} )</td>
</tr>
<tr>
<td>R47: ( O^+ \rightarrow O_2 + O + O )</td>
<td>( 3.2 \times 10^{-11} )</td>
</tr>
<tr>
<td>R48: ( O^+ \rightarrow N_2 + O + N_2 )</td>
<td>( 1.8 \times 10^{-11} )</td>
</tr>
<tr>
<td>R49: ( O^+ \rightarrow M + O_2 + M )</td>
<td>( 7.4 \times 10^{-12} )</td>
</tr>
<tr>
<td>R50: ( O^+ \rightarrow O_2 + O + O )</td>
<td>( 5.2 \times 10^{-12} )</td>
</tr>
<tr>
<td>R51: ( O + O_2 \rightarrow O_3 + O )</td>
<td>( k_0 = 2.8 \times 10^{-12} )</td>
</tr>
<tr>
<td>R52: ( O + O_2 \rightarrow O_3 + O_2 )</td>
<td>( 5.95 \times 10^{-12} )</td>
</tr>
<tr>
<td>R53: ( O + N_2 \rightarrow O + N_2 )</td>
<td>( 2.8 \times 10^{-12} )</td>
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<tr>
<td>R54: ( O + O_2 \rightarrow O_3 + O )</td>
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<tr>
<td>R55: ( O + O_2 \rightarrow O_3 + CO )</td>
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<tr>
<td>R56: ( O + CO \rightarrow O_2 + CO )</td>
<td>( 3.0 \times 10^{-14} )</td>
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<tr>
<td>R57: ( O + CO \rightarrow O_3 + CO )</td>
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<td>R59: ( O + CO \rightarrow O_3 + CO )</td>
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<td>R83: ( O + CO \rightarrow O_3 + CO )</td>
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<tr>
<td>R84: ( O + CO \rightarrow O_3 + CO )</td>
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Table A1 (continued)

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<td>( R_{26} )</td>
<td>( k_{\text{R}} = 1.0 \times 10^{-11} )</td>
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References


