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Photochemical synthesis of ammonia and amino acids from nitrous
oxide
Xiaofeng Zang¹*, Yuichiro Ueno¹,²,³, Norio Kitadai²,³

¹Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, Japan

²Earth-Life Science Institute (WPI-ELSI), Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

³Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Natsushima-cho, Yokosuka 237-0061, Japan

*Corresponding author:
Xiaofeng Zang
E-mail: zang.x.aa@m.titech.ac.jp
Tel: +81 80 3934 0892

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Abstract

Abiotic synthesis of ammonia and amino acids are important for origin of life and early evolution. Ammonia (NH₃) and organic nitrogen species may be possibly produced from nitrous oxide (N₂O), which is a second abundant nitrogen species in the atmosphere. Here, we report a new photochemical experiment and evaluate whether N₂O can be used as a nitrogen source for prebiotic synthesis in the atmosphere. We conducted a series of experiments using a gas mixture of N₂O+CO, N₂O+CO₂ or N₂O+H₂ with the presence of liquid water. The results demonstrated that NH₃, methyl amine (CH₃NH₂) and some amino acids such as glycine, alanine and serine can be synthesized through photochemistry from N₂O even without metal catalysts. NH₃ can be produced not only from CO+N₂O, but also from H₂+N₂O. Glycine can be synthesized from CH₃NH₂ and CO₂, which can be produced from N₂O and CO under UV irradiation. Our work demonstrated for the first time that N₂O could be an important nitrogen source and provide a new process for synthesizing ammonia and organic nitrogen species that was not considered previously. Contribution of organic synthesis from N₂O should therefore be considered when discussing the prebiotic chemistry on primitive Earth.
1. Introduction

Nitrogen is an essential element for the origin of life and its evolution. The famous Miller-Urey experiment demonstrated that key building blocks of life, such as amino acids, can be synthesized from a reducing atmosphere including NH$_3$, CH$_4$, H$_2$ and H$_2$O (Miller 1953, 1955; Miller and Urey 1959). However, as is widely accepted nowadays, primitive atmosphere was less reducing, containing carbon source as mostly CO$_2$ and nitrogen source as mostly N$_2$ (e.g., Walker 1977, 1985; Kasting 1993). It is far less efficient to synthesize organic nitrogen compounds from the N$_2$ dominate atmosphere (Schlesinger and Miller, 1983). Therefore, it is crucial to understand how NH$_3$ and organic nitrogen molecules can be produced from atmosphere when discussing the origin of life.

Abiotic ammonia formation has been discussed by both experimental and theoretical studies: reduction of NO$_2^-$ and NO$_3^-$ by aqueous iron (II) Fe$^{2+}$ (Summers and Chang, 1993) or by ferrous sulfide FeS under acidic conditions (Summers 2005), directly reduction of NO by FeS (Summers et al., 2012); released by decomposition of ammonium micas (Eugster 1966); reduction of N$_2$/NO$_2}$/NO$_3^-$ in typical hydrothermal systems by minerals catalysts (Brander et al., 1998, 2008; Schoonen and Xu 2001; Smirnov et al., 2008; Singireddy et al., 2012). These studies focus on NO$_x$ as an intermediate nitrogen species to synthesize ammonia, which can be produced from atmosphere N$_2$ by lightning and meteorite impact (Yung and Mcelroy, 1979; Chyba and Sagan, 1991; Nna Mvondo et al., 2005; Laneuville et al., 2018). On the other hand, nitrous oxide (N$_2$O) may also be alternative intermediate for ammonia formation, but has not been explored yet.

Prebiotic N$_2$O level in early atmosphere is largely uncertain, though Airapetian et al. (2016) suggested that N$_2$O could be efficiently produced (20 ~ 3000 ppbv) owing to high activity of young Sun. Nna Mvondo et al. (2001, 2005) demonstrated that N$_2$O can be produced abiotically by coronal discharge in N$_2$-CO$_2$ gas mixtures. It is noticed that N$_2$O is also produced by spark discharge of N$_2$-CO$_2$ atmosphere and subsequent photochemical process (Summers and Khare 2007), though the experiment of Summers and Khare (2007) did not analyze NH$_3$ and other products during the experiment. It is possible that N$_2$O could be a nitrogen source to synthesize NH$_3$/NO$_2^-$/NO$_3^-$ or other organic nitrogen species. However, there are no experimental studies where N$_2$O is the initial nitrogen source.

Abiotic source of amino acids by various kinds of energy source has been studied for long years. They include spark discharges (Miller 1953, 1955; Miller and Urey 1959),
irradiation by ultraviolet lights, comic rays and/or solar flare particles (Groth and Weyssenhoff 1960; Sagan and Khare 1971; Kobayashi et al., 1989; 1990; 1998; 1999; Takahashi et al., 1999; Utsumi and Thkahashi 1998), hydrothermal synthesis (Oro et al., 1959; Lowe et al., 1963) and shock heating by meteorite impacts (Bar-Nun et al., 1970). Previous studies of atmospheric UV synthesis of amino acids used hydrocarbon (CH$_4$ or C$_2$H$_6$) and NH$_3$ as starting materials, and have demonstrated the production of glycine, alanine and serine (Groth and Weyssenhoff 1960; Sagan and Khare 1971), though it is uncertain whether amino acid can be produced from N$_2$O.

Here, we report a new photochemical experiment and evaluate whether N$_2$O can be used as a nitrogen source to produce NH$_3$ and other organic nitrogen species. We conducted a series of experiments using a gas mixture of N$_2$O/CO or N$_2$O/CO$_2$ or N$_2$O/H$_2$ with the presence of liquid water under the irradiation of ultraviolet light. The results indicated that NH$_3$ and some amino acids can be synthesized through photochemistry from N$_2$O even without metal catalysts.

2. Materials and Methods

2.1 Photochemical experiment

Outline of experimental apparatus are illustrated in Figure 1. Experiments were conducted in a glass flask (457 mL) with two ports, one is connected to the vacuum line for introduction and extraction of gas sample, and the other is for injection of N$_2$O or N$_2$. The top of the flask is made of UV-grade synthetic quartz window, which is transparent for >175 nm photon.

Before the UV irradiation, 50 mL of doubly-distilled water was injected and frozen by liquid nitrogen for degassing impurity. After the freeze-pump-thaw cycle twice, CO or CO$_2$ was introduced into the flask from the vacuum line at 25°C and then 10 ccSTP of N$_2$O or N$_2$ gas was injected into the flask using a gas-tight syringe. After introducing the gas mixture, the flask was kept at 25°C using a water bath (MC-1, ASONE). An aliquot of gas phase (407 cc) was sampled from the vacuum line for measuring gas concentration before the UV irradiation (0h).

A high-pressure xenon arc lamp (Xe lamp: Cermax, CX-04E, output setting 20 A) is used for the UV source, which has solar-like UV spectrum (Figure 2). In the experiment (A), UV light was irradiated vertically from the top to the surface of liquid water, while in the experiment (B), the flask was horizontally placed with 20 mL water and UV light
was irradiated only into the gas phase. Experiment-1B was conducted to figure out whether NH$_4^+$ and amino acids were produced from reactions in gas phase or in aqueous phase. During the irradiation, water temperature typically increasing up to 40˚C.

After the irradiation (1h, 3h, 5h, 8h, or 12.5h), the flask was cooled and kept at 25˚C, and then gas sample was collected from the vacuum line using a stainless steel finger (1.16 mL). After the collection of gas sample, remaining liquid in the flask was fully collected after each experiment.

2.2 Quantitative analysis of gas phase

Gas samples were analyzed by gas chromatograph (GC-4000, GL Sciences) equipped with two detectors; pulsed discharge detector (PDD) and thermal conductivity detector (TCD). The GC housed an initial 2 m column packed with SHINCARBON-ST (2.2 mm I.D.) and a second 2 m Haysep Q column (2.2 mm I.D.). Pure helium gas is used as the carrier gas.

Speciation and concentrations in the gas sample were determined by the retention time and peak area compared with known amount of standard gas, including pure CO, CO$_2$, H$_2$ and N$_2$O gas (>99.5%, GL Sciences) and mixed standard gas (N$_2$ 93.954%, CH$_4$ 0.996%, C$_2$H$_6$ 1.01%, n-C$_3$H$_8$ 1.01%, i-C$_3$H$_8$ 1.01%, CO$_2$ 1.01%, GL Sciences).

2.3 Quantitative analysis of dissolved species

Products dissolved in liquid sample were analyzed by high performance liquid chromatography (HPLC, Shimadzu) equipped with 4 different columns:

Organic acids were measured by the HPLC system equipped with an electric conductivity detector and an anion exchange column (Shin-pack SCR-102H, Shimadzu) at 40˚C. The p-Toluene sulfonic acids aqueous solution (5 mM) was used as the eluent at a rate of 1.6 ml min$^{-1}$.

Inorganic anion was measured by the HPLC system equipped with a suppressed conductivity detector and an anion exchange column (IC SI-90 4E, Shodex) at 40˚C. A mixture of 1.8 mM Na$_2$CO$_3$ and 1.7 mM NaHCO$_3$ aqueous solution was used as the solvent at a rate of 1.6 ml min$^{-1}$.

Ammonia was measured by the HPLC system equipped with an electric conductivity detector and an anion exchange column (Shin-pack IC-C4, Shimadzu) at 40˚C. The oxalic acids aqueous solution (2.5 mM) was used as the eluent at a rate of 1.0 ml min$^{-1}$.
Amino acids were quantified by another HPLC system (JASCO) equipped with a fluorescence detector and an ion exchange column (AApak Na II-S2, JASCO) at 40°C.

For determining retention time and calibration curve, we used following standard reagents: mixed aqueous solutions containing sodium formate HCOONa (98.0%, Wako), sodium acetate CH₃COONa·3H₂O (99.0%, Wako), glycolic acid C₂H₂O₃ (99%, Sigma-Aldrich) and glyoxylic acid monohydrate C₂H₃O₂·H₂O (98.0%, Sigma-Aldrich), sodium nitrite NaNO₂ (98.5%, Wako), sodium nitrate NaNO₃ (99.0%, Wako), ammonium chloride NH₄Cl (99.5%, Wako), glycine H₂NCH₂COOH (PEPTIDE INSTITUTE), β-alanine (PEPTIDE INSTITUTE), and serine (PEPTIDE INSTITUTE).

3. Results

Results of all experiments are showed in Table 1.

3.1 Experiment of N₂O+CO+H₂O(A)

In gas phase, both N₂O and CO were consumed, while H₂, N₂, CO₂ were formed as major products, and CH₄ was determined after 5 hours’ irradiation. Meanwhile, O₂ was below the detection limit. In aqueous phase, organic acids such as formic acid HCOOH, acetic acid CH₃COOH, glycolic acid CH₂(OH)COOH and glyoxylic acid CHOCOOH were produced. And NH₄⁺, methylamine as well as amino acids such as glycine, β-alanine and serine were determined. NO₂⁻ and NO₃⁻ were below the detection limit. Chromatogram of amino acids can be seen in Appendix.

For organic acids, formic acid was main product with 3.1% yield against the starting CO. The NH₄⁺ yield against initial N₂O was about 2.3% and glycine yield was about 0.05% (0.05% against initial CO), respectively. The yields of each species based on initial CO or initial N₂O as a function of irradiation time are showed in Figure 3.

3.2 Experiment of N₂O+CO+H₂O (B)

Product species in gas phase were similar to those in experiment (A) except β-alanine, which was below the detection limit in experiment (B). The yields of each species against initial CO or initial N₂O as a function of irradiation time are showed in Figure 3 as well. Compared with experiment (A), yields of formic acid and NH₄⁺ were of the same digit, while yields of acetate acid, glycine and serine were only 1/10 of those in experiment A.

3.3 Experiment of N₂O +H₂O
When CO was not included in initial gas mixture, N\textsubscript{2} and O\textsubscript{2} were produced in gas phase when N\textsubscript{2}O was consumed. On the other hand, NH\textsubscript{4}\textsuperscript{+} was below the detection limit in aqueous phase, instead oxidizing species such as NO\textsubscript{2} and NO\textsubscript{3} were produced. This indicated that NH\textsubscript{4}\textsuperscript{+} cannot be produced simply through photolysis of N\textsubscript{2}O and H\textsubscript{2}O and that CO contribute to the formation of NH\textsubscript{3} in experiment N\textsubscript{2}O+CO+H\textsubscript{2}O.

3.4 Experiment of N\textsubscript{2}+CO+H\textsubscript{2}O

When nitrogen source was changed to N\textsubscript{2}, no N-bearing species other than N\textsubscript{2} were detected in gas phase or aqueous phase. Meanwhile, CO\textsubscript{2}, H\textsubscript{2}, and CH\textsubscript{4} were produced in gas phase, and the same kinds of organic acids detected in experiment of N\textsubscript{2}O+CO+H\textsubscript{2}O were produced in aqueous phase. These organic molecules were considered to be produced from photolysis of CO and H\textsubscript{2}O.

3.5 Experiment of N\textsubscript{2}O+CO\textsubscript{2}+H\textsubscript{2}O

When carbon source was changed to less reducing gas like CO\textsubscript{2}, which is thought to be the main composition of primitive atmosphere of Earth and Mars, only N\textsubscript{2} and O\textsubscript{2} were produced in gas phase while N\textsubscript{2}O was consumed, no other N-bearing species or organic acids were detected. This experiment once again indicated that prebiotic chemistry favors reducing atmosphere than neutral or oxidizing atmosphere.

3.6 Experiment of N\textsubscript{2}+CO\textsubscript{2}+H\textsubscript{2}O

Gas mixture in this experiment is widely considered to be the main composition of primitive atmosphere. But no N-bearing species or organic molecules were detected.

4. Discussion

4.1 Production of main gas species

In our experiment, CO\textsubscript{2} and N\textsubscript{2} were the two most abundant species produced from CO and N\textsubscript{2}O under the presence of water. The CO\textsubscript{2} is formed mainly through the following reactions (Calvert and Pitts, 1966; DeMore et al., 1992):

\[ \text{H}_2\text{O} + h\nu (< 180\text{nm}) \rightarrow \text{H} + \text{OH} \quad [R1] \]
\[ \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad [R2] \]

On the other hand, N\textsubscript{2} are formed from the photolysis of N\textsubscript{2}O through the following
reactions (Preston and Barr, 1971; Schmidt et al., 2011):

\[
\text{N}_2\text{O} + h\nu (< 250\text{nm}) \rightarrow \text{N}_2 + \text{O}^1\text{D} \quad [\text{R3}]
\]

It is known that the N\(_2\)O is further reacted with O\(^1\)D to form NO (Prakash et al., 2005):

\[
\text{N}_2\text{O} + \text{O}^1\text{D} \rightarrow \text{N}_2 + \text{O}_2 \\
\rightarrow \text{NO} + \text{NO} \quad [\text{R4a}]
\]

\[
\rightarrow \text{NO} \quad [\text{R4b}]
\]

Photolysis rates of H\(_2\)O and N\(_2\)O can be estimated from production rates of CO\(_2\) and N\(_2\), respectively, using the reactions R1-R4. The production of NO could initiate the chain reactions to form HNO\(_2\), HNO\(_3\), NH\(_3\) and organic nitrogen compounds.

4.2 Synthesis of C\(_1\) compounds

In our study, amino acids may have been produced from organic acids or aldehydes. It is important to understand the key reactions to form C-H-O species as an amino acid precursor. When CO is the only carbon source, the reaction between CO and H radicals should initiate organic synthesis, which produce formyl radical (HCO) and then formaldehyde (HCHO) through the following reactions (Hikida et al., 1971; Ahumada et al., 1972; Bar-Nun and Chang 1983; Hochanadel et al., 1980; Pavlov et al., 2001):

\[
\text{CO} + \text{H} + \text{M} \rightarrow \text{HCO} + \text{M} \quad [\text{R5}]
\]

\[
\text{HCO} + \text{HCO} \rightarrow \text{HC} + \text{HCO} + \text{CO} \quad [\text{R6}]
\]

where M represents any third body collision partner. Once the HCO and HCHO formed, radical chain reactions can produce a number of organic carbon species.

In the gas phase, formic acid (HCOOH) could be produced by oxidation of formaldehyde (Yetter et al., 1989):

\[
\text{HCHO} + \text{OH} \rightarrow \text{HCOOH} + \text{H} \quad [\text{R7}]
\]

The formaldehyde also reacts with H and produce molecular hydrogen (H\(_2\)), methoxy radical (CH\(_3\)O), methanol (CH\(_3\)OH), methyl radical (CH\(_3\)) and methane (CH\(_4\)) (Baulch et al., 1992, 1994; Yung et al., 1988):

\[
\text{HCHO} + \text{H} \rightarrow \text{H}_2 + \text{HCO} \quad [\text{R8}]
\]

\[
\text{HCHO} + \text{H} + \text{M} \rightarrow \text{CH}_3\text{O} + \text{M} \quad [\text{R9}]
\]

\[
\text{CH}_3\text{O} + \text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H} \quad [\text{R10}]
\]

\[
\text{CH}_3\text{OH} + h\nu (160-200\text{nm}) \rightarrow \text{HCHO} + \text{H}_2 \\
\rightarrow \text{CH}_3\text{O} + \text{H} \quad [\text{R11a}]
\]

\[
\rightarrow \text{CH}_3 + \text{OH} \quad [\text{R11b}]
\]

\[
\rightarrow \text{CH}_2\text{OH} + \text{H} \quad [\text{R11d}]
\]

\[
\rightarrow \text{CH}_3 + \text{OH} \quad [\text{R11c}]
\]
\[ \text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H} \]  

[R12]

The CH\(_4\) reacts back into CH\(_3\)OH and CH\(_3\) in our system:

\[ \text{CH}_4 + \text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH} + \text{CH}_3 \]  

[R13]

Although the CH\(_3\)OH was not measured in our experiment, CH\(_4\) is likely produced from the above mechanism.

### 4.3 Synthesis of C\(_2\) compounds

It is hard to determine the exact photochemical mechanism to form various C\(_2\) compounds, though following reactions are possible to make C-C-bounding:

\[ \text{CH}_3 + \text{HCO} + \text{M} \rightarrow \text{CH}_3\text{CHO} + \text{M} \]  

[R14]

\[ \text{HCO} + \text{HCO} + \text{M} \rightarrow (\text{CHO})_2 + \text{M} \]  

[R15]

where CH\(_3\)CHO and (CHO\(_2\)) represents acetaldehyde and glyoxal, respectively. Similar to the oxidation of formaldehyde (R7), acetic acid (CH\(_3\)COOH) can also be produced by oxidation of acetaldehyde:

\[ \text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{COOH} + \text{H} \]  

[R16]

Similarly, glyoxylic acid (CHO\(_x\)COOH) can be formed by the same OH oxidation process from glyoxal (CHO\(_2\)):

\[ \text{CHOCHO} + \text{OH} \rightarrow \text{CHOCOOH} + \text{H} \]  

[R17]

Also, glycolic acid (HOCH\(_2\)COOH) could be synthesized from OH oxidation of glycolaldehyde (HOCH\(_2\)CHO), which could generate from CH\(_3\)OH radicals (R11d) combining with HCHO, as pointed out in Nuevo et al. (2010):

\[ \text{CH}_2\text{OH} + \text{HCHO} \rightarrow \text{HOCH}_2\text{CHO} + \text{H} \]  

[R8]

\[ \text{HOCH}_2\text{CHO} + \text{OH} \rightarrow \text{HOCH}_2\text{COOH} + \text{H} \]  

[R19]

### 4.4 Formation of HNO\(_2\) and HNO\(_3\) from N\(_2\)O under oxidizing condition

In an oxidizing O-H-N system like N\(_2\)O+H\(_2\)O, main N-bearing products were HNO\(_2\) and HNO\(_3\). Both are considered to be synthesized via a key intermediate HNO in the gas phase or potentially in aqueous phase (Summers and Khare, 2007). Gas phase reaction pathway is considered to start from NO that generated from [R4b], it could combine with H radicals to form HNO:

\[ \text{NO} + \text{H} + \text{M} \rightarrow \text{HNO} + \text{M} \]  

[R20]

The HNO also reacts with H radicals to generate NO radicals so that NO can be supplied sustainably in the system:
HNO + H → NO + H₂  \[\text{R21}\]

Meanwhile, N₂O itself combining with H radicals could generate HNNO, which reacts with NO to form NO₂:

N₂O + H + M → HNNO + M  \[\text{R22}\]
HNNO + NO → NO₂ + HNN  \[\text{R23}\]

Then, HNO₂ as well as HNO₃ could be synthesized through reactions involving HNO, NO, and NO₂:

NO + OH + M → HNO₂ + M  \[\text{R24}\]
HNO + NO₂ → HNO₂ + NO  \[\text{R25}\]
HNO₂ + NO₂ → HNO₃ + NO  \[\text{R26}\]
NO₂ + OH + M → HNO₃ + M  \[\text{R27}\]

On the other hand, HNO₂ and HNO₃ could also be synthesized in aqueous phase once HNO produced from R20 dissolves in water. Then HNO dissociates to form N₃Oₓ⁻ species, which decay into products, as is showed in Mancinelli and McKay (1988) and Summers and Khare (2007):

HNO → H⁺ + NO⁻  \[\text{R28}\]
NO⁻ + NO → N₂O₂⁻  \[\text{R29}\]
N₃O₂⁻ + NO → N₃O₃⁻  \[\text{R30}\]
N₃Oₓ⁻ → NO₂⁻ + NO₃⁻ + N₂O  \[\text{R31}\]

### 4.5 Formation of ammonia from N₂O

If the system is rich in CO, the HNO can be produced mainly from NO reacting with HCO radicals rather than the reaction with H (R20):

NO + HCO → CO + HNO  \[\text{R32}\]

The rate constant of R32 is about 1.35×10⁻¹¹ cm³ molec⁻¹ s⁻¹ at room temperature (Dammeier et al., 2007), and in our experiment, estimated reaction rate of R32 is 1.89×10¹³ molec/(cm³ · s), which is 10 times faster than that of R20 (5.86×10¹² molec/(cm³ · s)). Then, the main N-bearing products should be HNO₂ and HNO₃ via reaction pathways from [R21] to [R31] discussed in section 4.4. However, in the experiment of N₂O+CO+H₂O, HNO₂ and HNO₃ were not detected either in (A) or in (B) (Table 1, Fig. 2). Instead, NH₄⁺ and other reducing N-bearing species such as amino acids were produced.

The production pathway to form NH₄⁺ from N₂O is largely uncertain. A possible
route to form NH$_3$ is starting from N atom produced predominantly from photodissociation of NO:

\[ \text{NO} + h\nu \rightarrow \text{N} + \text{O} \quad \text{[R33]} \]

Then, N atom may combine with H or H$_2$ to generate NH, NH$_2$ and NH$_3$:

\[ \text{N} + \text{H} + \text{M} \rightarrow \text{NH} + \text{M} \quad \text{[R34]} \]

\[ \text{N} + \text{H}_2 + \text{M} \rightarrow \text{NH}_2 + \text{M} \quad \text{[R35]} \]

\[ \text{NH}_2 + \text{H} + \text{M} \rightarrow \text{NH}_3 + \text{M} \quad \text{[R36]} \]

In order to test this possibility, we constructed a photochemical model including all reactions mentioned above and over 300 related reactions based on NIST database (Version 7.0) to run a numerical calculation under the same initial conditions of experiment N$_2$O+CO+H$_2$O. Reactions included in the model are listed in Appendix. In this model, produced NH$_3$ are assumed to be dissolved into the liquid water and thus escaped from photodissociation. As a result, however, the model yields only small amount of NH$_3$ (Fig. 4a), which is much less than the experimental results (Fig. 4b), although the amount of major species (CO$_2$, N$_2$, H$_2$) was consistent with the experiment. In the model, produced HNO$_2$ and HNO$_3$ were much larger than NH$_3$. The model results indicate that the reaction pathway from R33 to R36 is not a major route to form NH$_3$, which is produced through additional mechanism not considered in the model.

One of the possible explanations is that our photochemical model only considered reactions in gas phase, yet NH$_3$ formation driven by UV partly takes place in aqueous solution. If so, when UV light was only irradiated to the gas phase, the amount of NH$_3$ should be less than experiment N$_2$O+CO+H$_2$O (A). With this thought, additional experiment (N$_2$O+CO+H$_2$O (B)) was designed to irradiate UV horizontally and thus avoid UV chemistry in the solution. However, as is showed in Fig.2, the production of NH$_4^+$ in the experiment (B) was of the same order of that in the experiment N$_2$O+CO+H$_2$O(A). This result indicates that UV chemistry in aqueous phase is not important to produce and that NH$_3$ could be produced in the gas phase. In actual experiment, dissolution of NH$_3$ into liquid water may prohibit further loss of ammonia by photo-dissociation.

Alternatively, presence of CO may contribute to the formation of NH$_3$. In order to figure out if CO is involved in the reaction pathway to produce NH$_3$, we conduct UV experiments starting from N$_2$O and H$_2$ with liquid water (EXP-6A, Table 2). The results show that both oxidizing products (NO$_2^-$ and NO$_3^-$) and reducing product (NH$_4^+$) were
produced during the first 5 hours, and after 8 hours’ irradiation, only NH$_4^+$ was detected. These results demonstrated that NH$_3$ can be synthesized without CO and other carbon species. For the ammonium formation, both CO and H$_2$ may work as reducing agents.

### 4.6 Formation of amino acids

In the experiment N$_2$O+CO+H$_2$O, methyamine (CH$_3$NH$_2$) and simple amino acids such as glycine, serine and β-alanine were produced. It is noticed that when UV-light is irradiated only to the gas phase (experiment B), the product yields of CH$_3$NH$_2$ and amino acids are 10 times less than that when UV-light is irradiated to liquid phase (experiment A) as is showed in Fig2. This difference could be explained by either because they were destroyed by UV light before they escape to the water in experiment B, or amino acids are synthesized in aqueous phase rather than in gas phase.

Nishizawa and Egami (1982) pointed out a route to synthesize α-amino acids through N-acyl amino acids, which can be produced from NH$_3$ and glyoxylic acid as follows:

$$2\text{CHO-COOH} + \text{NH}_3 \rightarrow \text{HOOC-CO-NH-CH}_2\text{-COOH}$$

$$\overset{\text{H}_2\text{O}^+}{\text{+}} \text{Gly} + (\text{COOH})_2$$  \[\text{R37}\]

this reaction could occur even at room temperature under UV irradiation in neutral or weak acidic aqueous solution and obtain a 20% yield. In our experiment, the amount of NH$_3$ and glyoxylic acid is 10 times more than that of glycine, and initial solution is neutral, thus it is possible that glycine could also be synthesized through [R37] in aqueous solution.

We conducted a control experiment starting from mixture solution of 1 mM NH$_3$ and 5 mM glycolic acid, with N$_2$ or CO filled in the gas phase to see whether this reaction could actually happen under our experimental conditions. The results showed that glycine was formed only when the gas phase contained CO (EXP-7A~10A, Table 3), yet the product yield of glycine was only about 0.0021% of the initial glyoxylic acid, which cannot completely explain the production amount of glycine in the experiment of N$_2$O+CO+H$_2$O. In the experiment of NH$_3$+glycolic acid, the initial pH of solution is 2.92, in such strong acidic solution reaction [R37] can be negligible. Thus, UV irradiation to mixed solution of NH$_3$ glycolic acid is not efficient to synthesize glycine in our experiment. The amino acids were not produced mainly from NH$_3$ but from N$_2$O and/or its derivatives. This is also supported by an additional experiment started from CO + NH$_3$
On the other hand, glycine may also be produced from CH$_3$NH$_2$ and CO$_2$, which is demonstrated experimental study mimicking interstellar UV reaction on ice grain (Holtom et al., 2005; Bossa et al., 2009; Lee et al., 2009; Suzuki et al., 2016; Aponte et al., 2017). It may be possible that under the solar-like UV CO$_2$ can addict to CH$_3$NH$_2$ to synthesize glycine by the following reaction:

\[
\text{CH}_3\text{NH}_2 + \text{CO}_2 \rightarrow \text{NH}_2\text{-CH}_2\text{-COOH} \quad \text{[R38]}
\]

In our experiment, CO$_2$ is the main product in gas and CH$_3$NH$_2$ is the second abundant products of N-bearing species in aqueous solution. The CO$_2$ and CH$_3$NH$_2$ could be combined to synthesize glycine. To test the reaction [R38], we conducted an additional UV experiment using 1.0 mM CH$_3$NH$_2$ · HCl solution (initial pH=7.60) and CO$_2$ gas. As a result, about 1.6% of starting CH$_3$NH$_2$ was converted into glycine after 12 h (EXP-12A, Table 4.). In this experiment, production of glycine was on going at 12h and not equilibrated, though the >1.6% conversion may be comparable to those in the N$_2$O+CO+H$_2$O experiment (Table 1). Therefore, [R38] could be the main route of the glycine formation, although it is largely uncertain for the production of the other minor amino acids (serine and alanine).

5. Conclusions

Our experiments demonstrated a new process for the first time that NH$_3$ as well as simple amino acids such as glycine, serine and alanine can be synthesized from gas mixture of N$_2$O, CO and H$_2$O by solar-like photochemistry without catalyst. They can be produced in gas phase, and could be protected from photolytic destruction in liquid water.

The mechanism of NH$_3$ formation is largely uncertain, though N$_2$O can be converted into NH$_3$ when appropriate reducing agent (CO or H$_2$) is available. Although we examine a few possible reaction pathways to form NH$_3$, the production mechanism of NH$_3$ is not yet explained quantitatively. There may be other unknown reactions to generate NH$_3$ in gas phase, or NH$_3$ could be produced by reduction from NO$_2^-$ and NO$_3^-$ via aqueous reactions.

On the other hand, glycine could be formed through the CO$_2$ addiction to CH$_3$NH$_2$, which can be produced from N$_2$O and CO under solar-live UV irradiation. In addition, glycine may possibly be produced from glyoxylic acid and ammonia (Nishizawa and Egami, 1982), though the route is not the main reaction in our UV experiment.
Previously, N₂O has not been considered as a main nitrogen source that could generate building blocks of life on primitive Earth, where amino acids have been considered to come from lightning of N₂ atmosphere, hydrothermal production and/or from space by meteorite impact. Atmospheric synthesis from N₂O could be an additional or even more efficient process to provide amino acids. The atmospheric N₂O level in early atmosphere is largely uncertain, though potentially 10 times higher than today (Airapetian et al., 2016). Therefore, photochemical production of organic matters from N₂O should be considered when discussing the chemical evolution before the first life arose. Our study demonstrated that N₂O could be an important nitrogen source and could provide a new process for synthesizing organic nitrogen species that was not considered before.

Acknowledgement
The authors thank W. Kawade and Y. Endo for support in conducting experiments and in the discussion. This work was financially supported by JSPS Kakenhi 17H01176 and 16H04073 for Y.U.
References
Eugster H. P., and Munoz J. (1966) Ammonium Micas: Possible Sources of Atmospheric


Schlesinger G., and Miller S. (1983) Prebiotic synthesis in atmospheres containing CH\(_4\), CO and


Figure 1. Outline of experimental apparatus. (A) UV light irradiated vertically from the top to the surface of liquid water; (B) UV light irradiated horizontally, only into the gas phase.

Figure 2. The spectrum of Xe lamp used in the experiments, which is close to the natural sunlight to simulate the ultraviolet light from the Sun.
Figure 3. Products yields relative to initial carbon (above) or initial nitrogen (below) as a function of irradiation time (min). (A-1) and (A-2) show results of the experiment N$_2$O+CO+H$_2$O(A), (B-1) and (B-2) show results of the experiment N$_2$O+CO+H$_2$O(B). The Y axis are scaled logarithmically.
Figure 4. Results of numerical calculation compared with experimental results. (a) shows the calculation results of our photochemical model, and (b) shows the results of UV experiment of N$_2$O+CO+H$_2$O (b). The Y axis are scaled logarithmically.

Table 1. Results of UV experiments

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time [min]</th>
<th>H$_2$O Flask [mL]</th>
<th>Gas (Initial gas species [mM])</th>
<th>Final gas species [mM]</th>
<th>Final dissolved species [mM]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>60</td>
<td>439</td>
<td>380</td>
<td>1399</td>
<td>N.d.</td>
</tr>
<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>180</td>
<td>439</td>
<td>380</td>
<td>1342</td>
<td>n.d.</td>
</tr>
<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>300</td>
<td>439</td>
<td>390</td>
<td>1062</td>
<td>n.d.</td>
</tr>
<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>480</td>
<td>439</td>
<td>380</td>
<td>1400</td>
<td>n.d.</td>
</tr>
<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>750</td>
<td>449</td>
<td>399</td>
<td>1771</td>
<td>n.d.</td>
</tr>
<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>60</td>
<td>439</td>
<td>410</td>
<td>1219</td>
<td>n.d.</td>
</tr>
<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>180</td>
<td>439</td>
<td>410</td>
<td>1224</td>
<td>n.d.</td>
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<td>N$_2$O+CO+H$_2$O</td>
<td>300</td>
<td>439</td>
<td>400</td>
<td>1505</td>
<td>n.d.</td>
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<td>439</td>
<td>410</td>
<td>1240</td>
<td>n.d.</td>
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<td>N$_2$O+CO+H$_2$O</td>
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<td>439</td>
<td>410</td>
<td>1175</td>
<td>n.d.</td>
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<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>60</td>
<td>439</td>
<td>430</td>
<td>n.d.</td>
<td>611</td>
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<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>120</td>
<td>439</td>
<td>430</td>
<td>n.d.</td>
<td>518</td>
</tr>
<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>300</td>
<td>459</td>
<td>409</td>
<td>n.d.</td>
<td>788</td>
</tr>
<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>480</td>
<td>459</td>
<td>409</td>
<td>n.d.</td>
<td>973</td>
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<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>160</td>
<td>457</td>
<td>407</td>
<td>1700</td>
<td>n.d.</td>
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<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>300</td>
<td>457</td>
<td>407</td>
<td>1275</td>
<td>n.d.</td>
</tr>
<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>360</td>
<td>459</td>
<td>409</td>
<td>1591</td>
<td>n.d.</td>
</tr>
<tr>
<td>N$_2$O+CO+H$_2$O</td>
<td>720</td>
<td>459</td>
<td>409</td>
<td>1376</td>
<td>491</td>
</tr>
</tbody>
</table>

a: UV is simulated by the top in the experiment series A, whereas UV irradiated horizontally in the experiment series B, thus not reaching to the surface of liquid water.

b: Both N$_2$ and O$_2$ were detected, though not quantitatively measured because the two peaks were overlapped each other.

n.d.: Measured but not quantified

n.a.: Not analyzed.
Table 2. Results of UV experiments starting from N₂O and H₂ instead of CO.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>EXP-6A N₂O+H₂+H₂O</td>
<td>180</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>721</td>
<td>519</td>
<td>413</td>
</tr>
<tr>
<td>N₂O+H₂+H₂O</td>
<td>300</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>1258</td>
<td>947</td>
<td>1055</td>
</tr>
<tr>
<td>N₂O+H₂+H₂O</td>
<td>480</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>1900</td>
<td>438</td>
<td>1431</td>
</tr>
<tr>
<td>N₂O+H₂+H₂O</td>
<td>750</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>2098</td>
<td>735</td>
<td>1390</td>
</tr>
</tbody>
</table>

Table 3. Results of UV experiments starting from ammonium solution with glyoxylate acid or CO.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>EXP-7A Glyoxylate acid + NH₄Cl(aq) + N₂(g)</td>
<td>60</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>630</td>
</tr>
<tr>
<td>Glyoxylate acid + NH₄Cl(aq) + N₂(g)</td>
<td>180</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>695</td>
</tr>
<tr>
<td>Glyoxylate acid + NH₄Cl(aq) + CO(g)</td>
<td>300</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>680</td>
</tr>
<tr>
<td>EXP-8A Glyoxylate acid + NH₄Cl(aq) + CO(g)</td>
<td>60</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>858</td>
</tr>
<tr>
<td>Glyoxylate acid + NH₄Cl(aq) + CO(g)</td>
<td>240</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>1176</td>
</tr>
<tr>
<td>EXP-9A Glyoxylate acid + NH₄Cl(aq) + CO(g) No UV</td>
<td>1020</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>1069</td>
</tr>
<tr>
<td>EXP-10A Glyoxylate acid + NH₄Cl(aq) + CO(g)</td>
<td>180</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>464</td>
</tr>
<tr>
<td>EXP-11A CO + NH₄(aq)</td>
<td>60</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>2306</td>
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<tr>
<td>CO + NH₄(aq)</td>
<td>300</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>2148</td>
</tr>
<tr>
<td>CO + NH₄(aq)</td>
<td>480</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>2434</td>
</tr>
</tbody>
</table>

*: detectable but too little to be analyzed

Table 4. Results of UV experiments of CO₂ and CH₃NH₂.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>EXP-12A CH₃NH₂ + HCl(aq) + CO₂(g)</td>
<td>60</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>1764</td>
<td>48.0</td>
<td>n.d.</td>
</tr>
<tr>
<td>CH₃NH₂ + HCl(aq) + CO₂(g)</td>
<td>180</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>1351</td>
<td>48.0</td>
<td>n.d.</td>
</tr>
<tr>
<td>CH₃NH₂ + HCl(aq) + CO₂(g)</td>
<td>420</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>1346</td>
<td>48.0</td>
<td>n.d.</td>
</tr>
<tr>
<td>CH₃NH₂ + HCl(aq) + CO₂(g)</td>
<td>720</td>
<td>50</td>
<td>430</td>
<td>380</td>
<td>1548</td>
<td>48.0</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

n.a.: Not analyzed.
Appendix

Photochemical synthesis of ammonia and amino acids from nitrous oxide

Xiaofeng Zang¹*, Yuichiro Ueno¹,²,³, Norio Kitadai²,³

Figure: chromatogram of amino acids.

Table: List of chemical reactions used in our photochemical model.

<table>
<thead>
<tr>
<th>No</th>
<th>Rate Constant</th>
<th>Reaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>3.15E-06</td>
<td>H₂O ==&gt; H⁺OH</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R2</td>
<td>5.43E-08</td>
<td>CO₂ ==&gt; CO + O</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R3</td>
<td>5.95E-06</td>
<td>CO₂ ==&gt; CO + Od</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R4</td>
<td>1.01E-04</td>
<td>O₂ ==&gt; O + Od</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R5</td>
<td>1.93E-06</td>
<td>O₂ ==&gt; O + O</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R6</td>
<td>2.34E-01</td>
<td>O₃ ==&gt; Od + O₂</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R7</td>
<td>5.95E-02</td>
<td>O₃ ==&gt; O + O₂</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R8</td>
<td>2.20E-02</td>
<td>HO₂ ==&gt; OH + O</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R9</td>
<td>3.38E-03</td>
<td>H₂O₂ ==&gt; OH + OH</td>
<td>Wen et al. 2001</td>
</tr>
<tr>
<td>R10</td>
<td>1.95E-03</td>
<td>H₂CO ==&gt; H₂ + CO</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R11</td>
<td>2.35E-03</td>
<td>H₂CO ==&gt; HCO + H</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R12</td>
<td>4.02E-01</td>
<td>HCO ==&gt; CO + H</td>
<td>Pinto et al. 1980</td>
</tr>
<tr>
<td>-------</td>
<td>---------</td>
<td>----------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>R13</td>
<td>1.00E-30</td>
<td>HCOOH ==&gt; OH + HCO</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R14</td>
<td>4.88E-04</td>
<td>CH3OH ==&gt; CH3 + OH</td>
<td>Wen et al. 1989</td>
</tr>
<tr>
<td>R15</td>
<td>1.98E-03</td>
<td>CH3OH ==&gt; H2CO + H2</td>
<td>Wen et al. 1990</td>
</tr>
<tr>
<td>R16</td>
<td>1.98E-03</td>
<td>CH3OH ==&gt; CH3O + H</td>
<td>Wen et al. 1991</td>
</tr>
<tr>
<td>R17</td>
<td>1.00E-30</td>
<td>CH3COOH ==&gt; CH3CO + OH</td>
<td>Wen et al. 1992</td>
</tr>
<tr>
<td>R18</td>
<td>9.81E-03</td>
<td>CH2CO ==&gt; H2C + CO</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R19</td>
<td>2.59E-03</td>
<td>CH3CHO ==&gt; CH3 + HCO</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R20</td>
<td>2.59E-03</td>
<td>CH3CHO ==&gt; CH4 + CO</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R21</td>
<td>5.19E-03</td>
<td>C2H5CHO ==&gt; C2H5 + HCO</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R22</td>
<td>1.36E-03</td>
<td>CH2 ==&gt; C + H</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R23</td>
<td>7.52E-03</td>
<td>CH3 ==&gt; HCH + H</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R24</td>
<td>6.00E-34</td>
<td>O + O2 + A ==&gt; O3 + A</td>
<td>DeMore et al. 1997</td>
</tr>
<tr>
<td>R25</td>
<td>2.94E-33</td>
<td>O + O + A ==&gt; O2 + A</td>
<td>Javoy et al. 2003</td>
</tr>
<tr>
<td>R26</td>
<td>8.34E-15</td>
<td>O + O3 ==&gt; O2 + O2</td>
<td>Atkinson et al. 2004</td>
</tr>
<tr>
<td>R27</td>
<td>2.94E-18</td>
<td>O + H2 ==&gt; OH + H</td>
<td>Baulch et al. 1992</td>
</tr>
<tr>
<td>R28</td>
<td>1.63E-21</td>
<td>O + H2O ==&gt; OH + OH</td>
<td>Lifshitz et al. 1991</td>
</tr>
<tr>
<td>R29</td>
<td>2.20E-10</td>
<td>Od + H2O ==&gt; OH + OH</td>
<td>Dunlea et al. 2004</td>
</tr>
<tr>
<td>R30</td>
<td>2.60E-11</td>
<td>Od + A ==&gt; O + A</td>
<td>Sobral et al. 1993</td>
</tr>
<tr>
<td>R32</td>
<td>1.00E-10</td>
<td>Od + H2 ==&gt; OH + H</td>
<td>DeMore et al. 1997</td>
</tr>
<tr>
<td>R33</td>
<td>1.89E-12</td>
<td>OH + OH ==&gt; H2O + O</td>
<td>Atkinson et al. 2004</td>
</tr>
<tr>
<td>R34</td>
<td>6.97E-14</td>
<td>OH + O3 ==&gt; HO2 + O2</td>
<td>Atkinson et al. 2004</td>
</tr>
<tr>
<td>R35</td>
<td>3.25E-11</td>
<td>OH + O2 ==&gt; H + O2</td>
<td>Atkinson et al. 2004</td>
</tr>
<tr>
<td>R36</td>
<td>7.00E-15</td>
<td>OH + H2 ==&gt; H2O + H</td>
<td>Atkinson et al. 2004</td>
</tr>
<tr>
<td>R37</td>
<td>6.78E-31</td>
<td>H + OH + A ==&gt; H2O + A</td>
<td>Baulch et al. 1992</td>
</tr>
<tr>
<td>R38</td>
<td>5.50E-32</td>
<td>H + O2 + A ==&gt; HO2 + A</td>
<td>Atkinson et al. 2004</td>
</tr>
<tr>
<td>R40</td>
<td>6.48E-12</td>
<td>H + HO2 ==&gt; H2 + O2</td>
<td>Atkinson et al. 2004</td>
</tr>
<tr>
<td>R41</td>
<td>1.62E-12</td>
<td>H + HO2 ==&gt; H2O + O</td>
<td>Atkinson et al. 2004</td>
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<tr>
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<td>Atkinson et al. 2004</td>
</tr>
<tr>
<td>R43</td>
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<td>Rate Constant</td>
<td>Reaction</td>
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<td>---------------</td>
<td>----------</td>
<td>-----------</td>
</tr>
<tr>
<td>R44</td>
<td>8.89E-33</td>
<td>H+H+A⇒H2+A</td>
<td>Baulch et al.1992</td>
</tr>
<tr>
<td>R45</td>
<td>5.84E-11</td>
<td>HO2+O⇒OH+O2</td>
<td>Atkinson et al. 2004</td>
</tr>
<tr>
<td>R46</td>
<td>2.15E-15</td>
<td>HO2+O3⇒OH+O2+O2</td>
<td>Atkinson et al. 2004</td>
</tr>
<tr>
<td>R47</td>
<td>1.64E-12</td>
<td>HO2+HO2⇒H2O2+O2</td>
<td>DeMore et al. 1997</td>
</tr>
<tr>
<td>R48</td>
<td>1.78E-15</td>
<td>H2O2+O⇒OH+HO2</td>
<td>Atkinson et al. 2004</td>
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<tr>
<td>R49</td>
<td>1.70E-12</td>
<td>H2O2+OH⇒H2O2+H2O</td>
<td>Atkinson et al. 2004</td>
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<tr>
<td>R50</td>
<td>4.18E-14</td>
<td>H2O2+H⇒OH+H2O</td>
<td>Baulch et al.1992</td>
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<tr>
<td>R51</td>
<td>1.50E-13</td>
<td>CO+OH⇒CO2+H</td>
<td>Baulch et al.1992</td>
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<tr>
<td>R52</td>
<td>4.54E-36</td>
<td>CO+O+A⇒CO2+A</td>
<td>Tsang et al. 1986</td>
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<tr>
<td>R53</td>
<td>1.18E-34</td>
<td>CO+H+A⇒HCO+A</td>
<td>Baulch et al.1994</td>
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<td>R54</td>
<td>1.00E-10</td>
<td>HCO+O⇒H+CO2</td>
<td>Baulch et al.1992</td>
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<tr>
<td>R55</td>
<td>1.00E-10</td>
<td>HCO+O⇒OH+CO</td>
<td>Baulch et al.1992</td>
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<td>R56</td>
<td>5.62E-12</td>
<td>HCO+O2⇒H2O2+CO</td>
<td>Atkinson et al. 2004</td>
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<td>R57</td>
<td>1.20E-10</td>
<td>HCO+H⇒H2+CO</td>
<td>Pavlov et al. 2001</td>
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<td>R58</td>
<td>2.48E-21</td>
<td>HCO+H2⇒H2CO+H</td>
<td>Tsang et al.1986</td>
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<tr>
<td>R59</td>
<td>5.00E-11</td>
<td>HCO+OH⇒H2O+CO</td>
<td>Baulch et al.1992</td>
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<tr>
<td>R60</td>
<td>3.99E-22</td>
<td>HCO+A⇒CO+H+A</td>
<td>Friedrichs et al.2002</td>
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<td>R61</td>
<td>3.00E-11</td>
<td>HCO+HCO⇒H2CO+CO</td>
<td>Baulch et al.1992</td>
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<td>R62</td>
<td>1.64E-13</td>
<td>H2CO+O⇒HCO+OH</td>
<td>Baulch et al.1992</td>
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<tr>
<td>R63</td>
<td>8.34E-12</td>
<td>H2CO+OH⇒H2O+HCO</td>
<td>Atkinson et al. 2004</td>
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<td>R64</td>
<td>2.15E-13</td>
<td>H2CO+OH⇒HCO+OH</td>
<td>Yetter et al. 1989</td>
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<tr>
<td>R65</td>
<td>3.84E-15</td>
<td>H2CO+H⇒H2+HCO</td>
<td>Baulch et al.1994</td>
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<td>R66</td>
<td>3.00E-16</td>
<td>H2CO+H⇒CH3O</td>
<td>Curran et al. 2006</td>
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<td>R67</td>
<td>1.00E-17</td>
<td>H2CO+HCO⇒H3O+CO</td>
<td>Wen et al. 1989</td>
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<td>R68</td>
<td>3.00E-11</td>
<td>CH3O+OH⇒H2CO+H2O</td>
<td>Tsang et al. 1986</td>
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<td>R69</td>
<td>3.30E-11</td>
<td>CH3O+H⇒H2CO+H</td>
<td>Baulch et al.1994</td>
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<td>R70</td>
<td>1.50E-10</td>
<td>CH3O+HCO⇒CH3OH+CO</td>
<td>Tsang et al. 1986</td>
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<td>R71</td>
<td>1.15E-15</td>
<td>CH3O+H2⇒CH3OH+H</td>
<td>Tsang et al. 1986</td>
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<td>R72</td>
<td>3.57E-09</td>
<td>CH3O+H2⇒CH3OH+H</td>
<td>Jodkowski et al. 1999</td>
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<td>R73</td>
<td>5.04E-07</td>
<td>CH3O+CH4⇒CH3OH+CH3</td>
<td>Tsang et al. 1986</td>
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<td>R74</td>
<td>6.55E-20</td>
<td>CH3O+CO⇒CH3+CO2</td>
<td>Tsang et al. 1986</td>
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<tr>
<td>R75</td>
<td>1.27E-15</td>
<td>CH3OH+H⇒CH3O+H2</td>
<td>Warnatz,1984</td>
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<tr>
<td>R</td>
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<td>Reaction</td>
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<td>R76</td>
<td>6.16E-13</td>
<td>CH$_3$OH+OH$\rightarrow$CH$_3$O+H$_2$O</td>
<td>Warnatz, 1984</td>
</tr>
<tr>
<td>R77</td>
<td>6.70E-12</td>
<td>CH$_3$+OH$\rightarrow$CO+H$_2$+H$_2$</td>
<td>Fenimore et al., 1968</td>
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<tr>
<td>R78</td>
<td>4.43E-13</td>
<td>CH$_3$+OH$\rightarrow$CH$_3$O+H</td>
<td>Jasper et al., 2007</td>
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<td>R79</td>
<td>1.10E-10</td>
<td>CH$_3$+O$\rightarrow$H$_2$CO+H</td>
<td>Baulch et al., 1992</td>
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<tr>
<td>R80</td>
<td>4.00E-31</td>
<td>CH$_3$+O$_2$$\rightarrow$H$_2$CO+OH</td>
<td>Tsang et al., 1986</td>
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<tr>
<td>R81</td>
<td>2.59E-12</td>
<td>CH$_3$+O$_3$$\rightarrow$H$_2$CO+HO$_2$</td>
<td>DeMore et al., 1992</td>
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<tr>
<td>R82</td>
<td>6.36E-37</td>
<td>CH$_3$+CO+A$\rightarrow$CH$_3$CO+A</td>
<td>Baulch et al., 1994</td>
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<td>R83</td>
<td>5.93E-28</td>
<td>CH$_3$+H+A$\rightarrow$CH$_4$+A</td>
<td>Baulch et al., 1994</td>
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<td>R84</td>
<td>1.66E-16</td>
<td>CH$_3$+H$_2$CO$\rightarrow$CH$_4$+HCO</td>
<td>Baulch et al., 1994</td>
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<td>R85</td>
<td>2.01E-10</td>
<td>CH$_3$+HCO$\rightarrow$CH$_4$+CO</td>
<td>Tsang et al., 1986</td>
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<td>R86</td>
<td>5.78E-14</td>
<td>CH$_3$+H$_2$$\rightarrow$CH$_4$+H</td>
<td>Baulch et al., 1992</td>
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<tr>
<td>R87</td>
<td>3.00E-11</td>
<td>CH$_3$+HCO$\rightarrow$CH$_3$CHO</td>
<td>Tsang et al., 1986</td>
</tr>
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<td>R88</td>
<td>2.20E-26</td>
<td>CH$_3$+CH$_3$+A$\rightarrow$C$_2$H$_6$+A</td>
<td>Baulch et al., 1992</td>
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<tr>
<td>R89</td>
<td>5.00E-11</td>
<td>CH$_3$CO+O$\rightarrow$H$_2$CO+HCO</td>
<td>Zhnle, 1986</td>
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<tr>
<td>R90</td>
<td>1.10E-13</td>
<td>CH$_3$CO+H$\rightarrow$CH$_3$+HCO</td>
<td>Ohmori et al., 1989</td>
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<td>R91</td>
<td>5.92E-14</td>
<td>CH$_3$CO+H$\rightarrow$CH$_2$CO+H$_2$</td>
<td>Ohmori et al., 1989</td>
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<tr>
<td>R92</td>
<td>5.40E-11</td>
<td>CH$_3$CO+CH$_3$$\rightarrow$C$_2$H$_6$+CO</td>
<td>Adachi et al., 1981</td>
</tr>
<tr>
<td>R93</td>
<td>8.60E-11</td>
<td>CH$_3$CO+CH$_3$$\rightarrow$CH$_4$+CH$_2$CO</td>
<td>Adachi et al., 1981</td>
</tr>
<tr>
<td>R94</td>
<td>4.50E-11</td>
<td>CH$_3$CO+HCO$\rightarrow$CH$_3$CHO+CO</td>
<td>Tsang et al., 1986</td>
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<tr>
<td>R95</td>
<td>6.05E-14</td>
<td>CH$_2$CO+H$\rightarrow$CH$_3$+CO</td>
<td>Senosiain et al., 2006</td>
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<tr>
<td>R96</td>
<td>3.30E-13</td>
<td>CH$_2$CO+O$\rightarrow$H$_2$CO+CO</td>
<td>Miller et al., 1982</td>
</tr>
<tr>
<td>R97</td>
<td>2.23E-13</td>
<td>CH$_3$CHO+CH$_3$$\rightarrow$CH$_3$CO+CH$_4$</td>
<td>Baulch et al., 1992</td>
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<tr>
<td>R98</td>
<td>2.23E-13</td>
<td>CH$_3$CHO+H$\rightarrow$CH$_3$CO+H$_2$</td>
<td>Ohmori et al., 1989</td>
</tr>
<tr>
<td>R99</td>
<td>5.80E-13</td>
<td>CH$_3$CHO+O$\rightarrow$CH$_3$CO+OH</td>
<td>DeMore et al., 1997</td>
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<tr>
<td>R100</td>
<td>1.59E-11</td>
<td>CH$_3$CHO+OH$\rightarrow$CH$_3$CO+H$_2$O</td>
<td>Atkinson et al., 2001</td>
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<td>R101</td>
<td>5.16E-13</td>
<td>CH$_3$CHO+OH$\rightarrow$HCOOH+CH$_3$</td>
<td>Cameron et al., 2002</td>
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<tr>
<td>R102</td>
<td>3.44E-13</td>
<td>CH$_3$CHO+OH$\rightarrow$CH$_3$COOH+H</td>
<td>Cameron et al., 2002</td>
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<tr>
<td>R103</td>
<td>2.82E-13</td>
<td>HCOOH+OH$\rightarrow$H$_2$O+CO$_2$+H</td>
<td>Wine et al., 1985</td>
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<tr>
<td>R104</td>
<td>4.76E-18</td>
<td>CH$_4$+O$\rightarrow$CH$_3$+OH</td>
<td>Miyoshi et al., 1993</td>
</tr>
<tr>
<td>R105</td>
<td>1.28E-10</td>
<td>CH$_4$+Od$\rightarrow$CH$_3$+OH</td>
<td>DeMore et al., 1994</td>
</tr>
<tr>
<td>R106</td>
<td>2.25E-11</td>
<td>CH$_4$+Od$\rightarrow$H$_2$CO+H</td>
<td>DeMore et al., 1994</td>
</tr>
<tr>
<td>R107</td>
<td>6.60E-15</td>
<td>CH4+OH===&gt;CH3+H2O</td>
<td>Srinivasan et al. 2005</td>
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<td>R108</td>
<td>4.87E-10</td>
<td>CH+CH4===&gt;C2H4+H</td>
<td>Cyzewski et al. 2002</td>
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<tr>
<td>R109</td>
<td>1.84E-12</td>
<td>CH+CO2===&gt;HCO+CO</td>
<td>Beman et al. 1982</td>
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<tr>
<td>R110</td>
<td>1.40E-11</td>
<td>CH+H===&gt;C+H2</td>
<td>Grebe et al. 1982</td>
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<tr>
<td>R111</td>
<td>5.02E-30</td>
<td>CH+H2+A===&gt;CH3+A</td>
<td>Fulle et al. 1997</td>
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<tr>
<td>R112</td>
<td>9.50E-11</td>
<td>CH+O===&gt;CO+H</td>
<td>Baulch et al. 1992</td>
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<tr>
<td>R113</td>
<td>5.90E-11</td>
<td>CH+O2===&gt;CO+OH</td>
<td>Lichtin et al. 1984</td>
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<tr>
<td>R114</td>
<td>3.49E-19</td>
<td>HCH+CH4===&gt;CH3+CH3</td>
<td>Bohland et al. 1985</td>
</tr>
<tr>
<td>R115</td>
<td>1.00E-12</td>
<td>HCH+CO2===&gt;H2CO+CO</td>
<td>Tsang et al. 1986</td>
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<tr>
<td>R116</td>
<td>1.26E-11</td>
<td>HCH+H2===&gt;H2C+H2</td>
<td>Romani et al. 1993</td>
</tr>
<tr>
<td>R117</td>
<td>5.00E-15</td>
<td>HCH+H2===&gt;CH3+H</td>
<td>Tsang et al. 1986</td>
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<tr>
<td>R118</td>
<td>8.80E-12</td>
<td>HCH+A===&gt;H2C+A</td>
<td>Ashfold et al. 1981</td>
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<tr>
<td>R119</td>
<td>3.00E-11</td>
<td>HCH+O2===&gt;HCO+OH</td>
<td>Ashfold et al. 1981</td>
</tr>
<tr>
<td>R120</td>
<td>1.66E-18</td>
<td>HCH+OH===&gt;CH+H2O</td>
<td>Jasper et al. 2007</td>
</tr>
<tr>
<td>R121</td>
<td>1.25E-10</td>
<td>HCH+OH===&gt;CH2O+H</td>
<td>Jasper et al. 2007</td>
</tr>
<tr>
<td>R122</td>
<td>3.00E-11</td>
<td>H2C+C2H3===&gt;CH3+C2H2</td>
<td>Tsang et al. 1986</td>
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<tr>
<td>R123</td>
<td>3.00E-11</td>
<td>H2C+C2H5===&gt;CH3+C2H4</td>
<td>Tsang et al. 1986</td>
</tr>
<tr>
<td>R124</td>
<td>7.00E-11</td>
<td>H2C+CH3===&gt;C2H4+H</td>
<td>Tsang et al. 1986</td>
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<tr>
<td>R125</td>
<td>1.00E-28</td>
<td>H2C+CO+A===&gt;H2CO+A</td>
<td>Yung et al. 1988</td>
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<tr>
<td>R126</td>
<td>3.90E-14</td>
<td>H2C+CO2===&gt;H2CO+CO</td>
<td>Tsang et al. 1986</td>
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<tr>
<td>R127</td>
<td>1.37E-10</td>
<td>H2C+H===&gt;CH+H2</td>
<td>Baulch et al. 1992</td>
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<tr>
<td>R128</td>
<td>1.42E-29</td>
<td>H2C+H2+A===&gt;CH3+A</td>
<td>Gladstone et al. 1996</td>
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<td>R129</td>
<td>2.00E-10</td>
<td>H2C+O===&gt;CO+H+H</td>
<td>Baulch et al. 1994</td>
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<tr>
<td>R130</td>
<td>8.00E-12</td>
<td>H2C+O===&gt;CH+OH</td>
<td>Huebner et al. 1980</td>
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<tr>
<td>R131</td>
<td>8.30E-11</td>
<td>H2C+O===&gt;CO+H2</td>
<td>Baulch et al. 1994</td>
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<td>R132</td>
<td>1.00E-11</td>
<td>H2C+O===&gt;HCO+H</td>
<td>Huebner et al. 1980</td>
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<td>R133</td>
<td>3.37E-12</td>
<td>H2C+O2===&gt;HCO+OH</td>
<td>Baulch et al. 1994</td>
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<td>R134</td>
<td>1.01E-11</td>
<td>CH2O+OH===&gt;H2O+HCO</td>
<td>Baulch et al. 1994</td>
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<td>R135</td>
<td>1.73E-13</td>
<td>CH2O+O===&gt;OH+HCO</td>
<td>Baulch et al. 1994</td>
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<td>R136</td>
<td>5.71E-14</td>
<td>CH2O+H===&gt;H2+HCO</td>
<td>Baulch et al. 1994</td>
</tr>
<tr>
<td>R137</td>
<td>3.33E-05</td>
<td>N2O===&gt;N2+Od</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R138</td>
<td>7.40E-05</td>
<td>NO===&gt;N+O</td>
<td>Pavlov et al. 2001</td>
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<td>Reaction</td>
<td>Rate Constant</td>
<td>Reaction</td>
<td>Reference</td>
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<td>R139</td>
<td>2.34E-01</td>
<td>NO2 ===&gt; NO + O</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R140</td>
<td>6.84E-02</td>
<td>HNO2 ===&gt; NO + OH</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R141</td>
<td>4.62E-03</td>
<td>HNO3 ===&gt; NO2 + OH</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R142</td>
<td>6.84E-02</td>
<td>HNO ===&gt; NO + H</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R143</td>
<td>1.00E-30</td>
<td>NH3 ===&gt; NH2 + H</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R144</td>
<td>3.33E-03</td>
<td>NH ===&gt; N + H</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R145</td>
<td>3.33E-03</td>
<td>NH2 ===&gt; NH + H</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R146</td>
<td>1.53E-01</td>
<td>NH2 ===&gt; NHH</td>
<td>Pavlov et al. 2001</td>
</tr>
<tr>
<td>R147</td>
<td>6.71E-11</td>
<td>N2O + Od ===&gt; NO + NO</td>
<td>DeMore et al., 1997</td>
</tr>
<tr>
<td>R148</td>
<td>4.90E-11</td>
<td>N2O + Od ===&gt; N2 + O2</td>
<td>DeMore et al., 1997</td>
</tr>
<tr>
<td>R149</td>
<td>4.94E-34</td>
<td>N2O + H ===&gt; NO + NH</td>
<td>Bozzelli et al. 1994</td>
</tr>
<tr>
<td>R150</td>
<td>4.31E-18</td>
<td>N2O + H ===&gt; OH + N2</td>
<td>Arthru et al. 1997</td>
</tr>
<tr>
<td>R151</td>
<td>1.49E-17</td>
<td>N2O + H ===&gt; HNNO</td>
<td>Dian et al. 1995</td>
</tr>
<tr>
<td>R152</td>
<td>8.02E-19</td>
<td>N2O + OH ===&gt; HO2 + N2</td>
<td>Tsang et al. 1991</td>
</tr>
<tr>
<td>R154</td>
<td>3.86E-32</td>
<td>NO + H + A ===&gt; HNO + A</td>
<td>Tsang et al. 1991</td>
</tr>
<tr>
<td>R155</td>
<td>8.93E-32</td>
<td>NO + O + A ===&gt; NO2 + A</td>
<td>DeMore et al. 1997</td>
</tr>
<tr>
<td>R156</td>
<td>5.80E-15</td>
<td>NO + Od ===&gt; O2 + N</td>
<td>Blais 1985 (upper limit)</td>
</tr>
<tr>
<td>R157</td>
<td>8.84E-12</td>
<td>NO + HO2 ===&gt; NO2 + OH</td>
<td>Atkinson et al. 2004</td>
</tr>
<tr>
<td>R158</td>
<td>1.35E-11</td>
<td>NO + HCO ===&gt; CO + HNO</td>
<td>Dammeyer et al., 2007</td>
</tr>
<tr>
<td>R159</td>
<td>1.18E-29</td>
<td>NO + CH3 + A ===&gt; CH3NO + A</td>
<td>Jodkowski et al., 1993</td>
</tr>
<tr>
<td>R160</td>
<td>3.65E-12</td>
<td>NO + HCH ===&gt; HCN + OH</td>
<td>Fikri et al., 2001</td>
</tr>
<tr>
<td>R161</td>
<td>3.65E-11</td>
<td>NO + HCH ===&gt; H + HCNO</td>
<td>Fikri et al., 2001</td>
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<tr>
<td>R162</td>
<td>1.37E-10</td>
<td>NO + CH ===&gt; O + HCN</td>
<td>Bergeat et al., 1998</td>
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<tr>
<td>R163</td>
<td>3.99E-11</td>
<td>NO + CH ===&gt; H + NCO</td>
<td>Bergeat et al., 1998</td>
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<td>R164</td>
<td>1.33E-11</td>
<td>NO + CH ===&gt; HCO + N</td>
<td>Bergeat et al., 1998</td>
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<td>R165</td>
<td>2.00E-10</td>
<td>NO + CH ===&gt; CO + N</td>
<td>Geiger et al., 1999</td>
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<td>R166</td>
<td>1.40E-10</td>
<td>NO + CH ===&gt; OH + CN</td>
<td>Geiger et al., 1999</td>
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<tr>
<td>R167</td>
<td>1.54E-11</td>
<td>NO + NCO ===&gt; CO + N2O</td>
<td>Lin et al., 1993</td>
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<tr>
<td>R168</td>
<td>1.96E-11</td>
<td>NO + NCO ===&gt; CO2 + N2</td>
<td>Lin et al., 1993</td>
</tr>
<tr>
<td>R169</td>
<td>2.16E-15</td>
<td>NH + NH ===&gt; NH2 + N</td>
<td>Klippenstein et al., 2009</td>
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<td>R</td>
<td>Rate Constant</td>
<td>Reaction</td>
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<td>R170</td>
<td>1.44E-28</td>
<td>NH+NH+A===&gt;HNNH+A</td>
<td>Nicholas et al. 1986</td>
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<td>R171</td>
<td>1.16E-09</td>
<td>NH+NH====&gt;N2+H+H</td>
<td>Meaburn et al. 1968</td>
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<td>R172</td>
<td>3.67E-19</td>
<td>NH+NO===&gt;O+HNN</td>
<td>Bozzelli et al. 1994</td>
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<tr>
<td>R173</td>
<td>2.87E-11</td>
<td>NH+NO===&gt;N2O+H</td>
<td>Bozzelli et al. 1994</td>
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<td>R174</td>
<td>4.78E-12</td>
<td>NH+NO===&gt;OH+N2</td>
<td>Bozzelli et al. 1994</td>
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<td>R175</td>
<td>1.17E-20</td>
<td>NH+OH===&gt;NH2+O</td>
<td>Cohen et al. 1991</td>
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<td>R177</td>
<td>1.39E-12</td>
<td>NH+OH===&gt;H2O+N</td>
<td>Klippenstein et al. 2009</td>
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<td>R178</td>
<td>1.89E-11</td>
<td>NH+N===&gt;N2+H</td>
<td>Caridade et al. 2005</td>
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<td>R179</td>
<td>1.16E-10</td>
<td>NH+O===&gt;NO+H</td>
<td>Cohen et al. 1991</td>
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<td>R180</td>
<td>1.16E-11</td>
<td>NH+O===&gt;OH+N</td>
<td>Cohen et al. 1991</td>
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<td>R181</td>
<td>2.11E-24</td>
<td>NH+CH4===&gt;CH3+NH2</td>
<td>Xu et al. 1999</td>
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<td>R182</td>
<td>1.25E-32</td>
<td>N+N+A===&gt;N2+A</td>
<td>Knipovich et al. 1988</td>
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<td>R183</td>
<td>9.16E-33</td>
<td>N+O+A===&gt;NO+A</td>
<td>Campbell et al. 1973</td>
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<td>R184</td>
<td>1.89E-11</td>
<td>N+NH===&gt;N2+H</td>
<td>Caridade et al. 2005</td>
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<td>R185</td>
<td>5.02E-32</td>
<td>N+H+A===&gt;NH+A</td>
<td>Brown et al. 1973</td>
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<td>R186</td>
<td>2.92E-11</td>
<td>N+NO===&gt;N2+O</td>
<td>DeMore et al. 1997</td>
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<td>R187</td>
<td>4.70E-11</td>
<td>N+OH===&gt;NO+H</td>
<td>Baulch et al. 1994</td>
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<td>R188</td>
<td>1.66E-10</td>
<td>N+CH===&gt;CN+H</td>
<td>Brownsword et al. 1996</td>
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<td>R189</td>
<td>1.00E-05</td>
<td>N+CH3===&gt;H2NC+H</td>
<td>Cimas et al. 2006</td>
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<td>R190</td>
<td>1.00E-36</td>
<td>N+H2+A===&gt;NH2+A</td>
<td>Petrishchev et al. 1981</td>
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<td>R191</td>
<td>2.69E-34</td>
<td>N+CH4+A===&gt;CH3NH+A</td>
<td>Aleksandrov et al. 1989</td>
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<td>R192</td>
<td>2.51E-14</td>
<td>N+CH4===&gt;HCN+H2+H</td>
<td>Takahashi 1972</td>
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<td>R193</td>
<td>7.47E-11</td>
<td>NH2+O===&gt;H+HNO</td>
<td>Cohen et al. 1991</td>
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<td>R194</td>
<td>1.16E-11</td>
<td>NH2+O===&gt;OH+NH</td>
<td>Cohen et al. 1991</td>
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<td>R195</td>
<td>8.30E-12</td>
<td>NH2+O===&gt;H2+NO</td>
<td>Cohen et al. 1991</td>
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<td>R196</td>
<td>1.65E-14</td>
<td>NH2+NH===&gt;NH3+N</td>
<td>Klippenstein et al. 2009</td>
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<td>R197</td>
<td>1.70E-10</td>
<td>NH2+NH===&gt;HNHH+H</td>
<td>Klippenstein et al. 2009</td>
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<td>R198</td>
<td>2.06E-15</td>
<td>NH2+NH2===&gt;NH3+NH</td>
<td>Klippenstein et al. 2009</td>
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<td>R199</td>
<td>1.42E-29</td>
<td>HN2+H+A===&gt;NH3+A</td>
<td>Altinay et al. 2012</td>
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<td>R200</td>
<td>3.59E-12</td>
<td>HNO+NH2 ==&gt; NH3+NO</td>
<td>Xu et al. 2009</td>
</tr>
<tr>
<td>R201</td>
<td>2.38E-14</td>
<td>HNO+NH2 ==&gt; H+NH2NO</td>
<td>Xu et al. 2009</td>
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<tr>
<td>R202</td>
<td>3.84E-17</td>
<td>HNO+NH2 ==&gt; NH2NHO</td>
<td>Xu et al. 2009</td>
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<tr>
<td>R203</td>
<td>4.54E-18</td>
<td>NH2+H2 ==&gt; NH3+H</td>
<td>Mebel et al. 1999</td>
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<td>R204</td>
<td>1.24E-11</td>
<td>NH2+NO ==&gt; N2+H2O</td>
<td>Park et al. 1999</td>
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<tr>
<td>R205</td>
<td>1.37E-12</td>
<td>NH2+NO ==&gt; OH+HNN</td>
<td>Park et al. 1999</td>
</tr>
<tr>
<td>R206</td>
<td>1.72E-15</td>
<td>NH2+NH2OH ==&gt; NH3+NH2O</td>
<td>Klippstein et al. 2009</td>
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<td>R207</td>
<td>2.55E-14</td>
<td>NH2+NH2OH ==&gt; NH3+NH3</td>
<td>Klippstein et al. 2009</td>
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<td>R208</td>
<td>1.10E-21</td>
<td>NH2+H2O ==&gt; OH+NH3</td>
<td>Cohen et al. 1991</td>
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<tr>
<td>R209</td>
<td>3.19E-12</td>
<td>NH2+HNNH ==&gt; NH3+HNN</td>
<td>Linder et al. 1996</td>
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<tr>
<td>R211</td>
<td>3.92E-13</td>
<td>NH2+OH ==&gt; H2O+NH</td>
<td>Mousavipour et al. 2009</td>
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<td>R212</td>
<td>2.21E-33</td>
<td>NH2+OH ==&gt; H2+HNO</td>
<td>Mousavipour et al. 2009</td>
</tr>
<tr>
<td>R213</td>
<td>1.32E-36</td>
<td>NH2+OH ==&gt; H2+NOH</td>
<td>Mousavipour et al. 2009</td>
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<td>R214</td>
<td>8.01E-14</td>
<td>NH2+OH ==&gt; NH3+O</td>
<td>Mousavipour et al. 2009</td>
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<td>R216</td>
<td>1.75E-27</td>
<td>CH3+NH2+A ==&gt; CH3NH2+A</td>
<td>Jodkowski et al. 1995</td>
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<tr>
<td>R217</td>
<td>8.40E-17</td>
<td>CH3+NH2 ==&gt; CH4+NH</td>
<td>Xu et al. 1999</td>
</tr>
<tr>
<td>R218</td>
<td>8.63E-19</td>
<td>C2H5+NH2 ==&gt; C2H6+NH</td>
<td>Xu et al. 1999</td>
</tr>
<tr>
<td>R219</td>
<td>3.98E-21</td>
<td>CH4+NH2 ==&gt; CH3+NH3</td>
<td>Song et al. 2003</td>
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<td>R220</td>
<td>3.51E-16</td>
<td>HO2+NH2 ==&gt; H2O+NOH</td>
<td>Sumathi et al. 1996</td>
</tr>
<tr>
<td>R221</td>
<td>2.50E-16</td>
<td>HO2+NH2 ==&gt; H2O+HNO</td>
<td>Sumathi et al. 1998</td>
</tr>
<tr>
<td>R222</td>
<td>6.33E-18</td>
<td>HO2+NH2 ==&gt; NH3+O2</td>
<td>Sumathi et al. 1996</td>
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<td>R223</td>
<td>3.19E-11</td>
<td>HO2+NH2 ==&gt; OH+NH2O</td>
<td>Sumathi et al. 1996</td>
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<td>R224</td>
<td>5.25E-17</td>
<td>NH2+CH2O ==&gt; NH3+HCO</td>
<td>Li et al. 2002</td>
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<td>R225</td>
<td>5.85E-18</td>
<td>HCN+O→→CO+NH</td>
<td>Perry et al. 1985</td>
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<td>R226</td>
<td>4.99E-18</td>
<td>HCN+O→→H+NCO</td>
<td>Perry et al. 1985</td>
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<td>R227</td>
<td>1.70E-30</td>
<td>HCN+O→→CN+OH</td>
<td>Perry et al. 1985</td>
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<td>R228</td>
<td>4.72E-28</td>
<td>HCN+H→→CN+H2</td>
<td>Tsang et al. 1991</td>
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<tr>
<td>R229</td>
<td>4.28E-19</td>
<td>HCN+OH→→CN+H2O</td>
<td>Tsang et al. 1991</td>
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<td>R230</td>
<td>3.18E-22</td>
<td>HCN+OH→→CO+NH2</td>
<td>Miller et al. 1988</td>
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<td>R231</td>
<td>1.23E-36</td>
<td>HCN+HCO→→CH2O+CN</td>
<td>Feng et al. 1997</td>
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<td>R232</td>
<td>1.40E-10</td>
<td>CN+O→→CO+N</td>
<td>Andersson et al. 2003</td>
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<td>R233</td>
<td>1.66E-12</td>
<td>HNNO+OH→→NO+NHOH</td>
<td>Lin et al. 1992</td>
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<td>R234</td>
<td>2.90E-14</td>
<td>HNNO+NO→→N2+HNO2</td>
<td>Lin et al. 1992</td>
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<td>R235</td>
<td>2.16E-12</td>
<td>HNNO+NO→→NO2+HNN</td>
<td>Lin et al. 1992</td>
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<tr>
<td>R236</td>
<td>3.57E-14</td>
<td>HNO+NO2→→HNO2+NO</td>
<td>Tsang et al. 1991</td>
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<td>R237</td>
<td>1.04E-11</td>
<td>HNO+CH3→→CH4+NO</td>
<td>Choi et al. 2005</td>
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<tr>
<td>R238</td>
<td>3.20E-30</td>
<td>NO2+OH+A→→HNO3+A</td>
<td>Troe 2012</td>
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<tr>
<td>R239</td>
<td>3.63E-13</td>
<td>HNO3+NH2→→NH3+NO3</td>
<td>Xu et al. 2010</td>
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<td>R240</td>
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<td>NO2+OH+A→→HNO3+A</td>
<td>Troe 2012</td>
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<td>R241</td>
<td>4.09E-16</td>
<td>NO2+OH→→HO2+NO</td>
<td>Tsang et al. 1991</td>
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<td>R242</td>
<td>1.45E-10</td>
<td>NO2+CH→→HCO+NO</td>
<td>Tao et al. 2001</td>
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<td>R243</td>
<td>1.70E-11</td>
<td>NO3+O→→NO2+O2</td>
<td>Atkinson et al. 2004</td>
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<td>R244</td>
<td>2.59E-11</td>
<td>NO3+NO→→NO2+NO2</td>
<td>Atkinson et al. 2004</td>
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<td>R245</td>
<td>2.00E-11</td>
<td>NO3+OH→→NO2+HO2</td>
<td>Atkinson et al. 2004</td>
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<td>R246</td>
<td>2.51E-10</td>
<td>NH3+O→→OH+NH2</td>
<td>DeMore et al. 1997</td>
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<td>R247</td>
<td>1.18E-24</td>
<td>NH3+CH3→→CH4+NH2</td>
<td>Yu et al. 1998</td>
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<td>R248</td>
<td>1.58E-31</td>
<td>N2+CH→→CHN2</td>
<td>Le Picard et al. 1998</td>
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<td>R249</td>
<td>1.58E-31</td>
<td>N2+CH→→CHN2</td>
<td>Le Picard et al. 1998</td>
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<td>R250</td>
<td>3.32E-11</td>
<td>HO2+NCO→→HNCO+O2</td>
<td>He et al. 1993</td>
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<td>R251</td>
<td>5.70E-11</td>
<td>HO2+O→→OH+O2</td>
<td>Atkinson et al. 2004</td>
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<td>R252</td>
<td>5.70E-11</td>
<td>HO2+O→→OH+O2</td>
<td>Atkinson et al. 2004</td>
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<td>R253</td>
<td>5.33E-80</td>
<td>HO2+NO→→HOONO</td>
<td>Zhu et al. 2003</td>
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<td>R254</td>
<td>1.11E-14</td>
<td>HO2+NO→→O2+HNO</td>
<td>Howard 1979</td>
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<td>R255</td>
<td>8.86E-12</td>
<td>HO2+NO===&gt;OH+NO2</td>
<td>Atkinson et al. 2004</td>
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<td>R256</td>
<td>6.87E-12</td>
<td>HO2+H2O===&gt;OH+H2O</td>
<td>Lloyd 1974</td>
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<td>R257</td>
<td>3.80E-11</td>
<td>HNO+O===&gt;OH+NO</td>
<td>Inomata 1999</td>
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<td>R258</td>
<td>3.02E-11</td>
<td>HNO+HNO===&gt;NO+NH2OH</td>
<td>Lin et al. 1992</td>
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<td>R259</td>
<td>8.48E-12</td>
<td>HNO+HNO===&gt;N2O+H2O</td>
<td>Lin et al. 1992</td>
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<td>R260</td>
<td>1.12E-14</td>
<td>HNO+NH2OH===&gt;NH2OH+NO</td>
<td>Lin et al. 1992</td>
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<td>R261</td>
<td>2.14E-22</td>
<td>HNO+H===&gt;NH+OH</td>
<td>Cohen et al. 1991</td>
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<td>R262</td>
<td>5.68E-12</td>
<td>HNO+H===&gt;H2+NO</td>
<td>Tsang et al. 1991</td>
</tr>
<tr>
<td>R263</td>
<td>1.51E-11</td>
<td>HNO+OH===&gt;H2O+NO</td>
<td>Tsang et al. 1991</td>
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<td>R264</td>
<td>3.81E-19</td>
<td>HNO+CH3===&gt;CH3NO+H</td>
<td>Choi et al. 2005</td>
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<td>R265</td>
<td>4.49E-29</td>
<td>HNO+HCO===&gt;CO+NH2O</td>
<td>Xu et al. 2004</td>
</tr>
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<td>R266</td>
<td>4.47E-24</td>
<td>HNO+HCO===&gt;CO+NH2O</td>
<td>Xu et al. 2004</td>
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<td>R267</td>
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<td>HNO+HCO===&gt;CH2O+NO</td>
<td>Xu et al. 2004</td>
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<td>R268</td>
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<td>HNO+CH3O===&gt;CH3OH+NO</td>
<td>He et al. 1988</td>
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<td>R269</td>
<td>7.49E-14</td>
<td>NH2OH+OH===&gt;H2O+NH2OH</td>
<td>Klippenstein et al. 2009</td>
</tr>
<tr>
<td>R271</td>
<td>1.66E-12</td>
<td>NH2OH+H===&gt;H2+HNO</td>
<td>Lin et al. 1992</td>
</tr>
<tr>
<td>R272</td>
<td>1.66E-12</td>
<td>NH2OH+OH===&gt;H2O+HNO</td>
<td>Lin et al. 1992</td>
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<tr>
<td>R273</td>
<td>1.52E-05</td>
<td>NH2OH+HCO===&gt;CO+NH2OH</td>
<td>Xu et al. 2004</td>
</tr>
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<td>R274</td>
<td>1.85E-08</td>
<td>NH2OH+HCO===&gt;CO+H2+HNO</td>
<td>Xu et al. 2004</td>
</tr>
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<td>R275</td>
<td>1.64E-05</td>
<td>NH2OH+HCO===&gt;CH2O+HNO</td>
<td>Xu et al. 2005</td>
</tr>
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<td>R276</td>
<td>1.99E-11</td>
<td>HNO2+O===&gt;OH+NO2</td>
<td>Tsang et al. 1991</td>
</tr>
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<td>R277</td>
<td>6.43E-13</td>
<td>HNO2+H===&gt;H2O+NO</td>
<td>Hsu et al. 1997</td>
</tr>
<tr>
<td>R278</td>
<td>1.26E-11</td>
<td>HNO2+H===&gt;OH+HNO</td>
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<tr>
<td>R279</td>
<td>2.27E-12</td>
<td>HNO2+H===&gt;H2+NO2</td>
<td>Hsu et al. 1997</td>
</tr>
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<td>R280</td>
<td>6.00E-12</td>
<td>HNO2+OH===&gt;H2O+NO2</td>
<td>Atkinson et al. 2004</td>
</tr>
<tr>
<td>R281</td>
<td>3.23E-32</td>
<td>HNO2+HCO===&gt;CO+H2O+NO</td>
<td>Xu et al. 2004</td>
</tr>
<tr>
<td>R282</td>
<td>1.43E-51</td>
<td>HNO2+HCO===&gt;CH2O+NO2</td>
<td>Xu et al. 2004</td>
</tr>
<tr>
<td>R283</td>
<td>3.63E-13</td>
<td>HNO3+NH2===&gt;NH3+NO3</td>
<td>Xu et al. 2010</td>
</tr>
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<tr>
<td>R286</td>
<td>1.50E-20</td>
<td>HNO3+NO ===&gt; HNO2+NO2</td>
<td>Kaiser et al. 1977</td>
</tr>
<tr>
<td>R287</td>
<td>4.18E-11</td>
<td>CN+NCO ===&gt; CO+NCN</td>
<td>Tzeng et al. 2009</td>
</tr>
<tr>
<td>R288</td>
<td>1.69E-11</td>
<td>CN+O ===&gt; CO+N</td>
<td>Baulch et al. 1992</td>
</tr>
<tr>
<td>R289</td>
<td>8.05E-11</td>
<td>CN+NO2 ===&gt; NO+NCO</td>
<td>Park et al. 1993</td>
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<tr>
<td>R290</td>
<td>7.11E-12</td>
<td>CN+NO2 ===&gt; CO+N2O</td>
<td>Park et al. 1993</td>
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<td>R291</td>
<td>5.20E-12</td>
<td>CN+NO2 ===&gt; CO2+N2</td>
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<td>R292</td>
<td>1.60E-13</td>
<td>CN+NO ===&gt; CO+N2</td>
<td>Li et al. 1985</td>
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<td>R293</td>
<td>2.42E-11</td>
<td>CN+O2 ===&gt; O+NCO</td>
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<td>1.66E-16</td>
<td>CN+NH3 ===&gt; HCN+NH2</td>
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<td>CN+CH4 ===&gt; HCN+CH3</td>
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<td>R297</td>
<td>1.69E-13</td>
<td>CN+CH2O ===&gt; CN+HCO</td>
<td>Feng et al. 1997</td>
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