Photochemical synthesis of ammonia and amino acids from nitrous oxide

Xiaofeng Zang[1*], Yuichiro Ueno[1,2,3], Norio Kitadai[2,3]

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

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

[3] *Japan 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 (NH_3) and organic nitrogen species may be possibly produced from nitrous oxide (N_2O), which is a second abundant nitrogen species in the atmosphere. Here, we report a new photochemical experiment and evaluate whether N_2O can be used as a nitrogen source for prebiotic synthesis in the atmosphere. We conducted a series of experiments using a gas mixture of N_2O+CO, N_2O+CO_2 or N_2O+H_2 with the presence of liquid water. The results demonstrated that NH_3, methyl amine (CH_3NH_2) and some amino acids such as glycine, alanine and serine can be synthesized through photochemistry from N_2O even without metal catalysts. NH_3 can be produced not only from CO+N_2O, but also from H_2+N_2O. Glycine can be synthesized from CH_3NH_2 and CO_2, which can be produced from N_2O and CO under UV irradiation. Our work demonstrated for the first time that N_2O 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 N_2O 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_2O (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 or 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_2O) may also be alternative intermediate for ammonia formation, but has not been explored yet.

Prebiotic N_2O level in early atmosphere is largely uncertain, though Airapetian et al. (2016) suggested that N_2O could be efficiently produced (20 ~ 3000 ppbv) owing to high activity of young Sun. Nna Mvondo et al. (2001, 2005) demonstrated that N_2O can be produced abiotically by coronal discharge in N_2-CO_2 gas mixtures. It is noticed that N_2O 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_2O 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_2O 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_2H_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_2O.

Here, we report a new photochemical experiment and evaluate whether N_2O 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_2O/CO or N_2O/CO_2 or N_2O/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_2O 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_2O 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_2O 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 Hayesep 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_2O gas (>99.5%, GL Sciences) and mixed standard gas (N_2 93.954%, CH_4 0.996%, C_2H_6 1.01%, n-C_3H_8 1.01%, i-C_3H_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_2CO_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 $CH_3COONa{\cdot}3H_2O$ (99.0%, Wako), glycolic acid $C_2H_4O_3$ (99%, Sigma-Aldrich) and glyoxylic acid monohydrate $C_2H_2O_3{\cdot}H_2O$ (98.0%, Sigma-Aldrich), sodium nitrite $NaNO_2$ (98.5%, Wako), sodium nitrate $NaNO_3$ (99.0%, Wako), ammonium chloride NH_4Cl (99.5%, Wako), glycine H_2NCH_2COOH (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 N_2O+CO+H_2O(A)

In gas phase, both N_2O and CO were consumed, while H_2, N_2, CO_2 were formed as major products, and CH_4 was determined after 5 hours' irradiation. Meanwhile, O_2 was below the detection limit. In aqueous phase, organic acids such as formic acid HCOOH, acetic acid CH_3COOH, glycolic acid $CH_2(OH)COOH$ and glyoxylic acid CHOCOOH were produced. And NH_4^+, methylamine as well as amino acids such as glycine, β-alanine and serine were determined. NO_2^- and NO_3^- 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 NH_4^+ yield against initial N_2O 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 N_2O as a function of irradiation time are showed in Figure 3.

3.2 Experiment of N_2O+CO+H_2O (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 N_2O as a function of irradiation time are showed in Figure 3 as well. Compared with experiment (A), yields of formic acid and NH_4^+ 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 N_2O +H_2O

When CO was not included in initial gas mixture, N_2 and O_2 were produced in gas phase when N_2O was consumed. On the other hand, NH_4^+ was below the detection limit in aqueous phase, instead oxidizing species such as NO_2^- and NO_3^- were produced. This indicated that NH_4^+ cannot be produced simply through photolysis of N_2O and H_2O and that CO contribute to the formation of NH_3 in experiment $N_2O+CO+H_2O$.

3.4 Experiment of N_2+CO+H_2O

When nitrogen source was changed to N_2, no N-bearing species other than N_2 were detected in gas phase or aqueous phase. Meanwhile, CO_2, H_2, and CH_4 were produced in gas phase, and the same kinds of organic acids detected in experiment of $N_2O+CO+H_2O$ were produced in aqueous phase. These organic molecules were considered to be produced from photolysis of CO and H_2O.

3.5 Experiment of $N_2O+CO_2+H_2O$

When carbon source was changed to less reducing gas like CO_2, which is thought to be the main composition of primitive atmosphere of Earth and Mars, only N_2 and O_2 were produced in gas phase while N_2O 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 $N_2+CO_2+H_2O$

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_2 and N_2 were the two most abundant species produced from CO and N_2O under the presence of water. The CO_2 is formed mainly through the following reactions (Calvert and Pitts, 1966; DeMore et al., 1992):

$$H_2O + h\nu\ (< 180\text{nm}) \rightarrow H + OH \qquad [R1]$$

$$CO + OH \rightarrow CO_2 + H \qquad [R2]$$

On the other hand, N_2 are formed from the photolysis of N_2O through the following reactions (Preston and Barr, 1971; Schmidt et al., 2011):

$$N_2O + h\nu\ (< 250\text{nm}) \rightarrow N_2 + O(^1D) \qquad [R3]$$

It is known that the N_2O is further reacted with $O(^1D)$ to form NO (Prakash et al., 2005) :

$$N_2O + O(^1D) \rightarrow N_2 + O_2 \qquad [R4a]$$

$$\rightarrow NO + NO \qquad [R4b]$$

Photolysis rates of H_2O and N_2O 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 C1 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):

$$CO + H + M \rightarrow HCO + M \qquad [R5]$$

$$HCO + HCO \rightarrow HCHO + CO \qquad [R6]$$

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):

$$HCHO + OH \rightarrow HCOOH + H \qquad [R7]$$

The formaldehyde also reacts with H and produce molecular hydrogen (H_2), methoxy radical (CH_3O), methanol (CH_3OH), methyl radical (CH_3) and methane (CH_4) (Baulch et al., 1992, 1994; Yung et al., 1988):

$$HCHO + H \rightarrow H_2 + HCO \qquad [R8]$$

$$HCHO + H + M \rightarrow CH_3O + M \qquad [R9]$$

$$CH_3O + H_2 \rightarrow CH_3OH + H \qquad [R10]$$

$$CH_3OH + h\nu\ (160\text{-}200\text{nm}) \rightarrow HCHO + H_2 \qquad [R11a]$$

$$\rightarrow CH_3O + H \qquad [R11b]$$

$$\rightarrow CH_3 + OH \qquad [R11c]$$

$$\rightarrow CH_2OH + H \qquad [R11d]$$

$CH_3 + H_2 \rightarrow CH_4 + H$ [R12]

The CH_4 reacts back into CH_3OH and CH_3 in our system:

$CH_4 + CH_3O \rightarrow CH_3OH + CH_3$ [R13]

Although the CH_3OH was not measured in our experiment, CH_4 is likely produced from the above mechanism.

4.3 Synthesis of C2 compounds

It is hard to determine the exact photochemical mechanism to form various C2 compounds, though following reactions are possible to make C-C-bounding:

$CH_3 + HCO + M \rightarrow CH_3CHO + M$ [R14]

$HCO + HCO + M \rightarrow (CHO)_2 + M$ [R15]

where CH_3CHO and $(CHO)_2$ represents acetaldehyde and glyoxal, respectively. Similar to the oxidation of formaldehyde (R7), acetic acid (CH_3COOH) can also be produced by oxidation of acetaldehyde:

$CH_3CHO + OH \rightarrow CH_3COOH + H$ [R16]

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

$CHOCHO + OH \rightarrow CHOCOOH + H$ [R17]

Also, glycolic acid ($HOCH_2COOH$) could be synthesized from OH oxidation of glycolaldehyde ($HOCH_2CHO$), which could generate from CH_2OH radicals (R11d) combining with HCHO, as pointed out in Nuevo et al. (2010):

$CH_2OH + HCHO \rightarrow HOCH_2CHO + H$ [R8]

$HOCH_2CHO + OH \rightarrow HOCH_2COOH + H$ [R19]

4.4 Formation of HNO_2 and HNO_3 from N_2O under oxidizing condition

In an oxidizing O-H-N system like N_2O+H_2O, 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:

$NO + H + M \rightarrow HNO + M$ [R20]

The HNO also reacts with H radicals to generate NO radicals so that NO can be supplied sustainably in the system:

$$HNO + H \rightarrow NO + H_2 \qquad [R21]$$

Meanwhile, N_2O itself combining with H radicals could generate HNNO, which reacts with NO to form NO_2:

$$N_2O + H + M \rightarrow HNNO + M \qquad [R22]$$

$$HNNO + NO \rightarrow NO_2 + HNN \qquad [R23]$$

Then, HNO_2 as well as HNO_3 could be synthesized through reactions involving HNO, NO, and NO_2:

$$NO + OH + M \rightarrow HNO_2 + M \qquad [R24]$$

$$HNO + NO_2 \rightarrow HNO_2 + NO \qquad [R25]$$

$$HNO_2 + NO_2 \rightarrow HNO_3 + NO \qquad [R26]$$

$$NO_2 + OH + M \rightarrow HNO_3 + M \qquad [R27]$$

On the other hand, HNO_2 and HNO_3 could also be synthesized in aqueous phase once HNO produced from R20 dissolves in water. Then HNO dissociates to form $N_xO_x^-$ species, which decay into products, as is showed in Mancinelli and McKay (1988) and Summers and Khare (2007):

$$HNO \rightarrow H^+ + NO^- \qquad [R28]$$

$$NO^- + NO \rightarrow N_2O_2^- \qquad [R29]$$

$$N_2O_2^- + NO \rightarrow N_3O_3^- \qquad [R30]$$

$$N_xO_x^- \rightarrow NO_2^- + NO_3^- + N_2O \qquad [R31]$$

4.5 Formation of ammonia from N_2O

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):

$$NO + HCO \rightarrow CO + HNO \qquad [R32]$$

The rate constant of R32 is about 1.35×10^{-11} cm^3 $molec^{-1}$ s^{-1} at room temperature (Dammeier et al., 2007), and in our experiment, estimated reaction rate of R32 is 1.89×10^{13} molec/(cm^3 · s), which is 10 times faster than that of R20 (5.86×10^{12} molec/(cm^3 · s)). Then, the main N-bearing products should be HNO_2 and HNO_3 via reaction pathways from [R21] to [R31] discussed in section 4.4. However, in the experiment of N_2O+CO+H_2O, HNO_2 and HNO_3 were not detected either in (A) or in (B) (Table 1, Fig. 2). Instead, NH_4^+ and other reducing N-bearing species such as amino acids were produced.

The production pathway to form NH_4^+ from N_2O is largely uncertain. A possible route to form NH_3 is starting from N atom produced predominantly from photodissociation of NO:

$$NO + h\nu \rightarrow N + O \qquad [R33]$$

Then, N atom may combine with H or H_2 to generate NH, NH_2 and NH_3:

$$N + H + M \rightarrow NH + M \qquad [R34]$$

$$N + H_2 + M \rightarrow NH_2 + M \qquad [R35]$$

$$NH_2 + H + M \rightarrow NH_3 + M \qquad [R36]$$

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_2O+CO+H_2O. 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_2O+CO+H_2O (A). With this thought, additional experiment (N_2O+CO+H_2O (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_2O+CO+H_2O(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_2O 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_2O+CO+H_2O, methylamine (CH_3NH_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_3NH_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:

$$\text{2CHO-COOH} + NH_3 \rightarrow \text{HOOC-CO-NH-}CH_2\text{-COOH}$$

$$\xrightarrow{H_3O^+} \text{Gly} + (\text{COOH})_2 \qquad [\text{R37}]$$

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_2O+CO+H_2O. 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_2O and/or its derivatives. This is also supported by an additional experiment started from CO + NH_3

(EXP-11A, Table3), yielding no detectable amino acids.

On the other hand, glycine may also be produced from CH_3NH_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_3NH_2 to synthesize glycine by the following reaction:

$$CH_3NH_2 + CO_2 \rightarrow NH_2\text{-}CH_2\text{-}COOH \qquad [R38]$$

In our experiment, CO_2 is the main product in gas and CH_3NH_2 is the second abundant products of N-bearing species in aqueous solution. The CO_2 and CH_3NH_2 could be combined to synthesize glycine. To test the reaction [R38], we conducted an additional UV experiment using 1.0 mM $CH_3NH_2 \cdot HCl$ solution (initial pH=7.60) and CO_2 gas. As a result, about 1.6% of starting CH_3NH_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_2O+CO+H_2O 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_2O, CO and H_2O 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_2O 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_3NH_2, which can be produced from N_2O 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, N_2O 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 N_2 atmosphere, hydrothermal production and/or from space by meteorite impact. Atmospheric synthesis from N_2O could be an additional or even more efficient process to provide amino acids. The atmospheric N_2O 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 N_2O should be considered when discussing the chemical evolution before the first life arose. Our study demonstrated that N_2O could be an important nitrogen source and could provide a new process for synthesizing organic nitrogen species that was not considered before.

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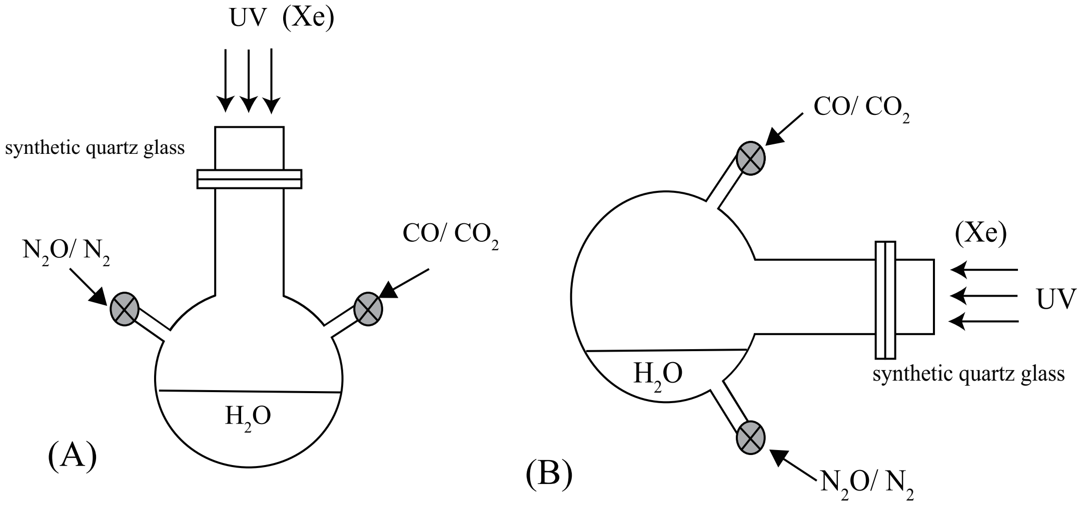

Figure 1. Outline of experimental apparatus. (A) UV light irradiated vertically from the top to the surface of liquid water; (B) UV light irradiated horizontally, only into the gas phase.

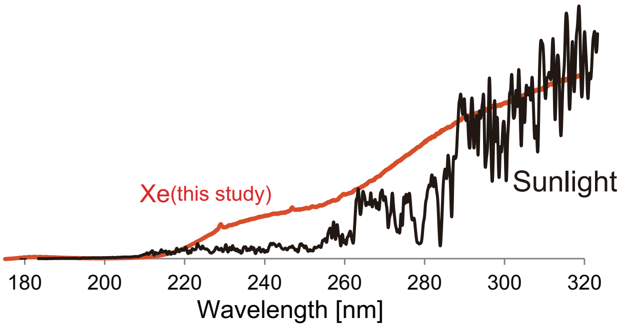

Figure 2. The spectrum of Xe lamp used in the experiments, which is close to the natural sunlight to simulate the ultraviolet light from the Sun.

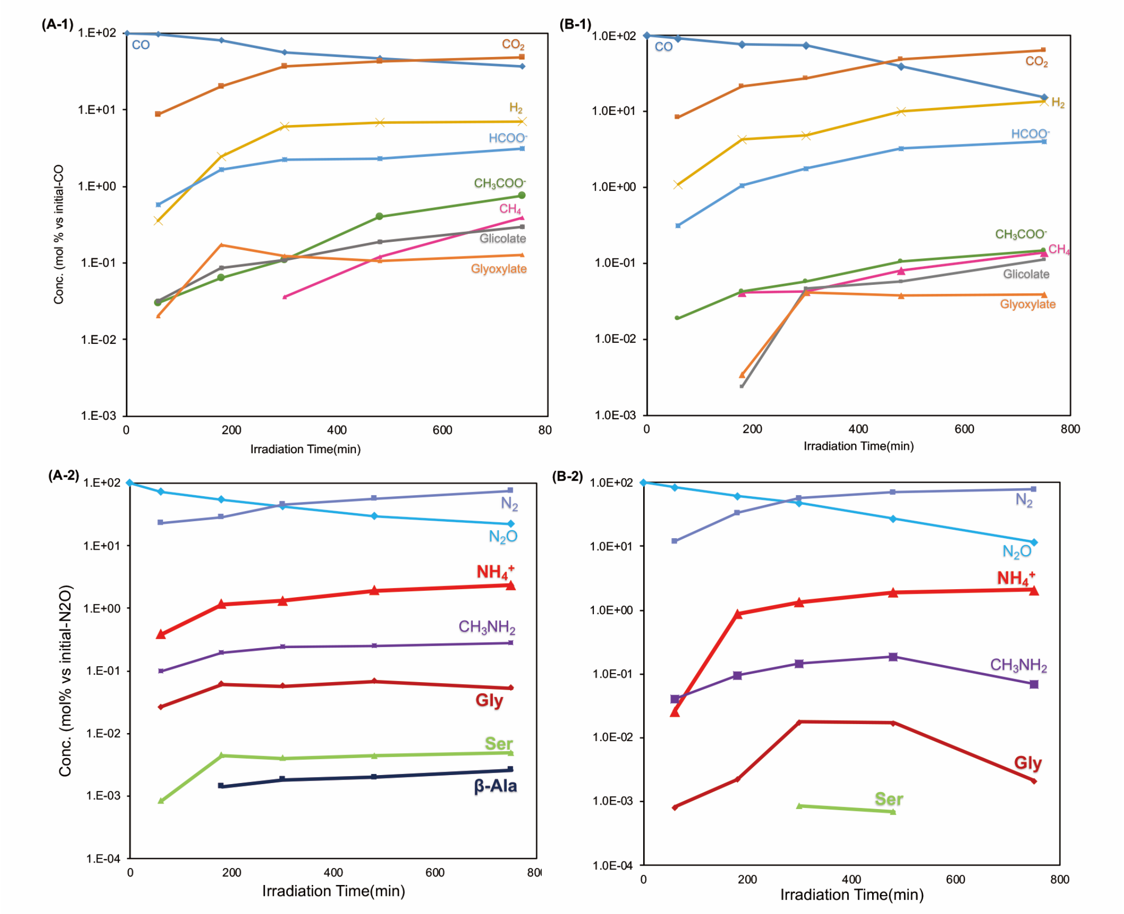

Figure 3. Products yields relative to initial carbon (above) or initial nitrogen (below) as a function of irradiation time (min). (A-1) and (A-2) show results of the experiment N_2O+CO+H_2O(A), (B-1) and (B-2) show results of the experiment N_2O+CO+H_2O(B). The Y axis are scaled logarithmically.

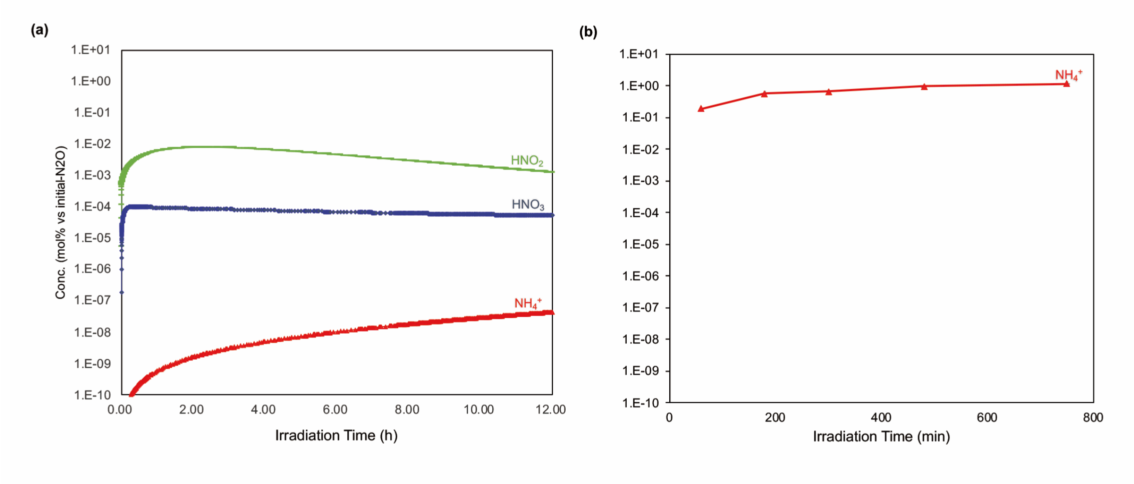

Figure 4. Results of numerical calculation compared with experimental results. (a) shows the calculation results of our photochemical model, and (b) shows the results of UV experiment of N_2O+CO+H_2O (b). The Y axis are scaled logarithmically.

Table 1. Results of UV experiments

Experiment [a]		Time	H_2O	Flask	Gas	Initial gas species [μmol]				Final gas species [μmol]							Final dissolved species [μmol]										
		[min.]	[ml]	[ml]	[ml]	CO	CO_2	N_2O	N_2	CO	CO_2	N_2O	N_2	O_2	H_2	CH_4	NO_2^-	NO_3^-	NH_4^+	Formate	Acetate	Glicolate	Glyoxylate	CH_3NH_2	Glycine	β-Alanin	Serine
EXP-1A	N_2O+CO+H_2O	60	50	430	380	1399	n.d.	470	n.d.	1357	121	343	110	n.d.	5.0	n.d.	n.d.	n.d.	1.81	8.02	0.21	0.22	0.14	0.46	0.124	n.d.	0.004
	N_2O+CO+H_2O	180	50	430	380	1342	n.d.	485	n.d.	1087	272	263	137	n.d.	33.1	n.d.	n.d.	n.d.	5.63	22.06	0.43	0.58	1.14	0.94	0.296	0.007	0.022
	N_2O+CO+H_2O	300	50	430	380	1062	n.d.	532	n.d.	596	386	226	242	n.d.	64.3	0.38	n.d.	n.d.	7.02	23.74	0.57	0.57	0.66	1.30	0.306	0.010	0.021
	N_2O+CO+H_2O	480	50	430	380	1406	n.d.	516	n.d.	669	608	154	297	n.d.	96.9	1.70	n.d.	n.d.	9.91	32.06	2.77	1.32	0.74	1.29	0.355	0.010	0.023
	N_2O+CO+H_2O	750	50	449	399	1771	n.d.	489	n.d.	659	847	107	365	n.d.	123.5	6.89	n.d.	n.d.	11.42	55.42	6.76	2.63	1.12	1.36	0.260	0.013	0.024
EXP-1B	N_2O+CO+H_2O	60	20	430	410	1219	n.d.	430	n.d.	1135	101	360	52	n.d.	13.2	n.d.	n.d.	n.d.	0.11	3.80	0.11	n.d.	n.d.	0.18	0.004	n.d.	n.d.
	N_2O+CO+H_2O	180	20	430	410	1224	n.d.	420	n.d.	932	262	254	144	n.d.	52.6	0.51	n.d.	n.d.	3.71	13.18	0.26	0.01	0.02	0.40	0.009	n.d.	n.d.
	N_2O+CO+H_2O	300	30	430	400	1505	n.d.	381	n.d.	1118	406	185	217	n.d.	74.0	0.64	n.d.	n.d.	5.16	26.89	0.43	0.36	0.31	0.57	0.067	n.d.	0.003
	N_2O+CO+H_2O	480	20	430	410	1243	n.d.	402	n.d.	485	608	110	290	n.d.	123.4	1.00	n.d.	n.d.	7.67	40.90	0.65	0.36	0.23	0.76	0.068	n.d.	0.003
	N_2O+CO+H_2O	750	20	430	410	1173	n.d.	420	n.d.	180	753	49	332	n.d.	158.6	1.62	n.d.	n.d.	8.73	47.00	0.86	0.65	0.23	0.29	0.009	n.d.	n.d.
EXP-2A	N_2O+H_2O	60	50	430	380	n.d.	n.d.	611	n.d.	n.d.	n.d.	519	-[b]		n.d.	n.d.	0.83	5.16	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	N_2O+H_2O	120	50	430	380	n.d.	n.d.	518	n.d.	n.d.	n.d.	443	-[b]		n.d.	n.d.	0.55	12.05	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	N_2O+H_2O	300	50	459	409	n.d.	n.d.	788	n.d.	n.d.	n.d.	224	-[b]		n.d.	n.d.	0.41	46.16	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	N_2O+H_2O	480	50	459	409	n.d.	n.d.	973	n.d.	n.d.	n.d.	470	-[b]		n.d.	n.d.	0.53	46.33	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
EXP-3A	N_2+CO+H_2O	160	50	457	407	1709	n.d.	n.d.	516	1325	142	n.d.	443	n.d.	54.1	n.d.	n.d.	n.d.	n.d.	11.71	0.28	2.37	1.12	n.d.	n.d.	n.d.	n.d.
	N_2+CO+H_2O	300	50	457	407	1275	n.d.	n.d.	579	778	308	n.d.	450	n.d.	119.6	1.13	n.d.	n.d.	n.d.	25.84	1.00	2.17	0.55	n.d.	n.d.	n.d.	n.d.
EXP-4A	N_2O+CO_2+H_2O	360	50	459	409	n.d.	1591	500	n.d.	n.d.	1301	140	-[b]		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	N_2O+CO_2+H_2O	720	50	459	409	n.d.	1389	497	n.d.	n.d.	1279	59	-[b]		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
EXP-5A	N_2+CO_2+H_2O	360	50	459	409	n.d.	1511	n.d.	478	n.d.	1349	n.d.	456	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	N_2+CO_2+H_2O	720	50	459	409	n.d.	1476	n.d.	491	n.d.	1403	n.d.	577	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

a: UV is irradiated from the top in the experiment series A, whereas UV irradiated horizontally in the experiment series B, thus not reached 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.

Experiment		Time	H_2O	Flask V	Gas V	Initial gas species [μmol]		Final gas species [μmol]				Final dissolved species [μmol]		
		[min.]	[ml]	[ml]	[ml]	H_2	N_2O	H_2	N_2O	N_2	O_2	NH_4^+	NO_2^-	NO_3^-
EXP-6A	N_2O+H_2+H_2O	180	50	430	380	721	519	413	296.7	296	n.d.	2.47	2.16	0.50
	N_2O+H_2+H_2O	300	50	430	380	1258	947	1055	532.2	692	n.d.	1.38	10.66	2.37
	N_2O+H_2+H_2O	480	50	430	380	1901	438	1431	1.3	490	n.d.	9.07	n.d.	n.d.
	N_2O+H_2+H_2O	750	50	430	380	2098	735	1390	0.7	903	n.d.	11.45	n.d.	n.d.

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

Experiment		Time	solution	Flask	Gas	Initial species [μmol]						Final dissolved species [μmol]							
		[min.]	[ml]	[ml]	[ml]	CO	N_2	Glyoxylate	NH_4^+	Glycine	pH	NH_4^+	Glyoxylate	Formate	Acetate	Glicolate	Oxalate	Glycine	pH
EXP-7A	Glyoxylic acid + NH_4Cl(aq)+ N_2(g)	60	50	430	380	n.d.	639	254.5	55.0	n.d.	2.92	55.5	115.6	34.12	n.d.	1.45	n.d.	n.d.	2.92
	Glyoxylic acid + NH_4Cl(aq)+ N_2(g)	180	50	430	380	n.d.	695	254.5	55.0	n.d.	2.92	55.9	20.9	44.52	1.09	2.69	n.d.	n.d.	
	Glyoxylic acid + NH_4Cl(aq)+ N_2(g)	300	50	430	380	n.d.	680	254.5	55.0	n.d.	2.92	55.4	2.5	36.50	4.46	2.66	n.d.	n.d.	3.15
EXP-8A	Glyoxylic acid + NH_4Cl(aq)+ CO(g)	60	50	430	380	858	n.d.	254.5	55.0	n.d.	2.92	55.5	115.5	36.06	n.d.	1.69	-[c]	0.0053	
	Glyoxylic acid + NH_4Cl(aq)+ CO(g)	240	50	430	380	1176	n.d.	254.5	55.0	n.d.	2.92	55.8	3.3	54.03	2.19	4.49	-[c]	0.0023	3.25
EXP-9A	Glyoxylic acid + NH_4Cl(aq)+ CO(g)_No UV	1020	50	430	380	1069	n.d.	254.5	55.4	n.d.	2.92	55.4	254.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.
EXP-10A	Glyoxylic acid + NH_4Cl(aq)+ CO(g)	180	50	430	380	464	n.d.	259.0	55.0	n.d.	9.43	n.a	217.2	14.26	n.d.	0.55	n.d.	0.3253	9.43
EXP-11A	CO + NH_3(aq)	60	50	430	380	2306	n.d.	n.d.	50.0	n.d.	9.93	n.a	n.d.	4.18	n.d.	0.38	n.d.	-[c]	8.31
	CO + NH_3(aq)	300	50	430	380	2148	n.d.	n.d.	50.0	n.d.	9.93	n.a	0.87	19.86	1.19	2.55	n.d.	-[c]	5.91
	CO + NH_3(aq)	480	50	430	380	2434	n.d.	n.d.	50.0	n.d.	9.93	n.a	0.61	33.26	2.18	2.74	n.d.	-[c]	4.53

c: detected but too little to be analyzed

Table 4. Results of UV experiments of CO_2 and CH_3NH_2.

Experiment		Time	solution	Flask	Gas	Initial species [μmol]				Initial pH	Final dissolved species [μmol]			Final pH
		[min.]	[ml]	[ml]	[ml]	CO_2	CH_3NH_2	NH_4^+	Glycine		CH_3NH_2	NH_4^+	Glycine	
EXP-12A	CH_3NH_2・HCl(aq)+ CO_2(g)	60	50	430	380	1764	48.0	n.d.	n.d.	7.60	47.3	2.59	0.189	5.93
	CH_3NH_2・HCl(aq)+ CO_2(g)	180	50	430	380	1351	48.0	n.d.	n.d.	7.60	45.7	4.16	0.440	5.81
	CH_3NH_2・HCl(aq)+ CO_2(g)	420	50	430	380	1346	48.0	n.d.	n.d.	7.60	38.3	12.3	0.485	n.a
	CH_3NH_2・HCl(aq)+ CO_2(g)	720	50	430	380	1548	48.0	n.d.	n.d.	7.60	43.4	7.12	0.747	5.35

n.a.: Not analyzed.

Appendix

Photochemical synthesis of ammonia and amino acids from nitrous oxide

Xiaofeng Zang[1*], Yuichiro Ueno[1,2,3], Norio Kitadai[2,3]

Figure: chromatogram of amino acids.

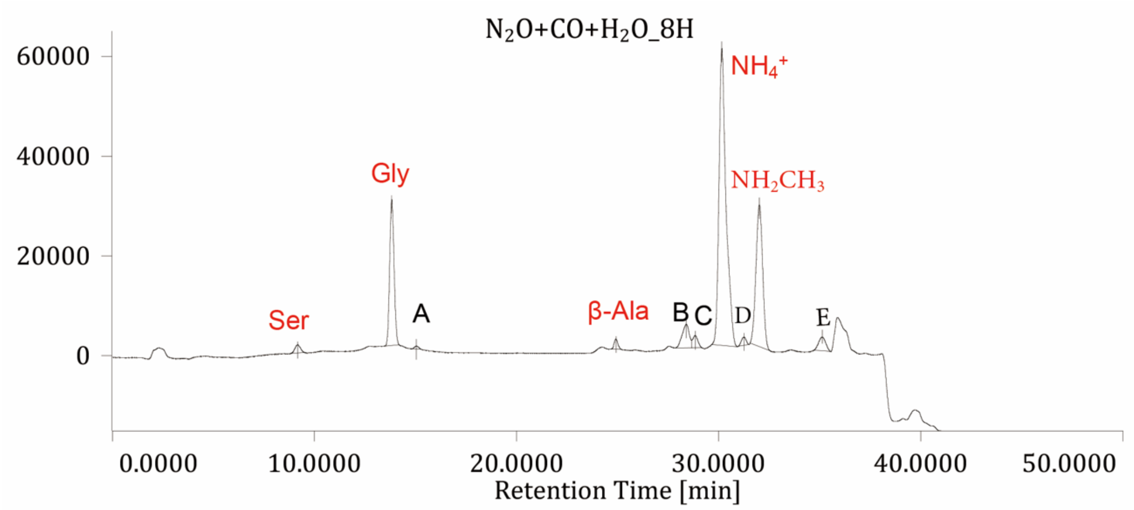

Table: List of chemical reactions used in our photochemical model.

No	Rate Constant	Reaction	Reference
R1	3.15E-06	H2O==>H+OH	Pavlov et al. 2001
R2	5.43E-08	CO2==>CO+O	Pavlov et al. 2001
R3	5.95E-06	CO2==>CO+Od	Pavlov et al. 2001
R4	1.01E-04	O2==>O+Od	Pavlov et al. 2001
R5	1.93E-06	O2==>O+O	Pavlov et al. 2001
R6	2.34E-01	O3==>Od+O2	Pavlov et al. 2001
R7	5.95E-02	O3==>O+O2	Pavlov et al. 2001
R8	2.20E-02	HO2==>OH+O	Pavlov et al. 2001
R9	3.38E-03	H2O2==>OH+OH	Wen et al. 2001
R10	1.95E-03	H2CO==>H2+CO	Pavlov et al. 2001
R11	2.35E-03	H2CO==>HCO+H	Pavlov et al. 2001

R12	4.02E-01	HCO==>CO+H	Pinto et al. 1980
R13	1.00E-30	HCOOH==>OH+HCO	Pavlov et al. 2001
R14	4.88E-04	CH3OH==>CH3+OH	Wen et al.1989
R15	1.98E-03	CH3OH==>H2CO+H2	Wen et al.1990
R16	1.98E-03	CH3OH==>CH3O+H	Wen et al.1991
R17	1.00E-30	CH3COOH==>CH3CO+OH	Wen et al.1992
R18	9.81E-03	CH2CO==>H2C+CO	Pavlov et al. 2001
R19	2.59E-03	CH3CHO==>CH3+HCO	Pavlov et al. 2001
R20	2.59E-03	CH3CHO==>CH4+CO	Pavlov et al. 2001
R21	5.19E-03	C2H5CHO==>C2H5+HCO	Pavlov et al. 2001
R22	1.36E-03	CH==>C+H	Pavlov et al. 2001
R23	7.52E-03	CH3==>HCH+H	Pavlov et al. 2001
R24	6.00E-34	O+O2+A==>O3+A	DeMore et al. 1997
R25	2.94E-33	O+O+A==>O2+A	Javoy et al.2003
R26	8.34E-15	O+O3==>O2+O2	Atkinson et al. 2004
R27	2.94E-18	O+H2==>OH+H	Baulch et al.1992
R28	1.63E-21	O+H2O==>OH+OH	Lifshitz et al.1991
R29	2.20E-10	Od+H2O==>OH+OH	Dunlea et al.2004
R30	2.60E-11	Od+A==>O+A	Sobral et al.1993
R31	4.04E-11	Od+O2==>O+O2	DeMore et al. 1997
R32	1.00E-10	Od+H2==>OH+H	DeMore et al. 1997
R33	1.89E-12	OH+OH==>H2O+O	Atkinson et al. 2004
R34	6.97E-14	OH+O3==>HO2+O2	Atkinson et al. 2004
R35	3.25E-11	OH+O==>H+O2	Atkinson et al. 2004
R36	7.00E-15	OH+H2==>H2O+H	Atkinson et al. 2004
R37	6.78E-31	H+OH+A==>H2O+A	Baulch et al. 1992
R38	5.50E-32	H+O2+A==>HO2+A	Atkinson et al. 2004
R39	2.92E-11	H+O3==>OH+O2	DeMore et al. 1997
R40	6.48E-12	H+HO2==>H2+O2	Atkinson et al. 2004
R41	1.62E-12	H+HO2==>H2O+O	Atkinson et al. 2004
R42	7.29E-11	H+HO2==>OH+OH	Atkinson et al. 2004
R43	3.00E-25	H+H2O==>OH+H2	Baulch et al.1992

R44	8.89E-33	H+H+A==>H2+A	Baulch et al.1992
R45	5.84E-11	HO2+O==>OH+O2	Atkinson et al. 2004
R46	2.15E-15	HO2+O3==>OH+O2+O2	Atkinson et al. 2004
R47	1.64E-12	HO2+HO2==>H2O2+O2	DeMore et al. 1997
R48	1.78E-15	H2O2+O==>OH+HO2	Atkinson et al. 2004
R49	1.70E-12	H2O2+OH==>HO2+H2O	Atkinson et al. 2004
R50	4.18E-14	H2O2+H==>OH+H2O	Baulch et al.1992
R51	1.50E-13	CO+OH==>CO2+H	Baulch et al.1992
R52	4.54E-36	CO+O+A==>CO2+A	Tsang et al. 1986
R53	1.18E-34	CO+H+A==>HCO+A	Baulch et al.1994
R54	1.00E-10	HCO+O==>H+CO2	Baulch et al.1992
R55	1.00E-10	HCO+O==>OH+CO	Baulch et al.1992
R56	5.62E-12	HCO+O2==>HO2+CO	Atkinson et al. 2004
R57	1.20E-10	HCO+H==>H2+CO	Pavlov et al. 2001
R58	2.48E-21	HCO+H2==>H2CO+H	Tsang et al.1986
R59	5.00E-11	HCO+OH==>H2O+CO	Baulch et al.1992
R60	3.99E-22	HCO+A==>CO+H+A	Friedrichs et al.2002
R61	3.00E-11	HCO+HCO==>H2CO+CO	Baulch et al.1992
R62	1.64E-13	H2CO+O==>HCO+OH	Baulch et al.1992
R63	8.34E-12	H2CO+OH==>H2O+HCO	Atkinson et al. 2004
R64	2.15E-13	H2CO+OH==>HCOOH+H	Yetter et al. 1989
R65	3.84E-15	H2CO+H==>H2+HCO	Baulch et al.1994
R66	3.00E-16	H2CO+H==>CH3O	Curran et al. 2006
R67	1.00E-17	H2CO+HCO==>CH3O+CO	Wen et al. 1989
R68	3.00E-11	CH3O+OH==>H2CO+H2O	Tsang et al. 1986
R69	3.30E-11	CH3O+H==>H2CO+H2	Baulch et al.1994
R70	1.50E-10	CH3O+HCO==>CH3OH+CO	Tsang et al. 1986
R71	1.15E-15	CH3O+H2CO==>CH3OH+HCO	Tsang et al. 1986
R72	3.57E-09	CH3O+H2==>CH3OH+H	Jodkowski et al. 1999
R73	5.04E-07	CH3O+CH4==>CH3OH+CH3	Tsang et al. 1986
R74	6.55E-20	CH3O+CO==>CH3+CO2	Tsang et al. 1986
R75	1.27E-15	CH3OH+H==>CH3O+H2	Warnatz ,1984

R76	6.16E-13	CH3OH+OH==>CH3O+H2O	Warnatz ,1984
R77	6.70E-12	CH3+OH==>CO+H2+H2	Fenimore et al.,1968
R78	4.43E-13	CH3+OH==>CH3O+H	Jasper et al.,2007
R79	1.10E-10	CH3+O==>H2CO+H	Baulch et al.1992
R80	4.00E-31	CH3+O2==>H2CO+OH	Tsang et al. 1986
R81	2.59E-12	CH3+O3==>H2CO+HO2	DeMore et al. 1992
R82	6.36E-37	CH3+CO+A==>CH3CO+A	Baulch et al.1994
R83	5.93E-28	CH3+H+A==>CH4+A	Baulch et al.1994
R84	1.66E-16	CH3+H2CO==>CH4+HCO	Baulch et al.1994
R85	2.01E-10	CH3+HCO==>CH4+CO	Tsang et al. 1986
R86	5.78E-14	CH3+H2==>CH4+H	Baulch et al.1992
R87	3.00E-11	CH3+HCO==>CH3CHO	Tsang et al. 1986
R88	2.20E-26	CH3+CH3+A==>C2H6+A	Baulch et al.1992
R89	5.00E-11	CH3CO+O==>H2CO+HCO	Zhnle, 1986
R90	1.10E-13	CH3CO+H==>CH3+HCO	Ohmori et al. 1989
R91	5.92E-14	CH3CO+H==>CH2CO+H2	Ohmori et al. 1989
R92	5.40E-11	CH3CO+CH3==>C2H6+CO	Adachi et al. 1981
R93	8.60E-11	CH3CO+CH3==>CH4+CH2CO	Adachi et al. 1981
R94	4.50E-11	CH3CO+HCO==>CH3CHO+CO	Tsang et al. 1986
R95	6.05E-14	CH2CO+H==>CH3+CO	Senosiain et al.2006
R96	3.30E-13	CH2CO+O==>H2CO+CO	Miller et al.1982
R97	2.23E-13	CH3CHO+CH3==>CH3CO+CH4	Baulch et al.1992
R98	2.23E-13	CH3CHO+H==>CH3CO+H2	Ohmori et al. 1989
R99	5.80E-13	CH3CHO+O==>CH3CO+OH	DeMore et al. 1997
R100	1.59E-11	CH3CHO+OH==>CH3CO+H2O	Atkinson et al.2001
R101	5.16E-13	CH3CHO+OH==>HCOOH+CH3	Cameron et al.2002
R102	3.44E-13	CH3CHO+OH==>CH3COOH+H	Cameron et al.2002
R103	2.82E-13	HCOOH+OH==>H2O+CO2+H	Wine et al. 1985
R104	4.76E-18	CH4+O==>CH3+OH	Miyoshi et al. 1993
R105	1.28E-10	CH4+Od==>CH3+OH	DeMore et al. 1994
R106	2.25E-11	CH4+Od==>H2CO+H2	DeMore et al. 1994

R107	6.60E-15	CH4+OH==>CH3+H2O	Srinivasan et al. 2005
R108	4.87E-10	CH+CH4==>C2H4+H	Cyzewski et al. 2002
R109	1.84E-12	CH+CO2==>HCO+CO	Beman et al. 1982
R110	1.40E-11	CH+H==>C+H2	Grebe et al. 1982
R111	5.02E-30	CH+H2+A==>CH3+A	Fulle et al. 1997
R112	9.50E-11	CH+O==>CO+H	Baulch et al.1992
R113	5.90E-11	CH+O2==>CO+OH	Lichtin et al. 1984
R114	3.49E-19	HCH+CH4==>CH3+CH3	Bohland et al. 1985
R115	1.00E-12	HCH+CO2==>H2CO+CO	Tsang et al. 1986
R116	1.26E-11	HCH+H2==>H2C+H2	Romani et al. 1993
R117	5.00E-15	HCH+H2==>CH3+H	Tsang et al. 1986
R118	8.80E-12	HCH+A==>H2C+A	Ashfold et al. 1981
R119	3.00E-11	HCH+O2==>HCO+OH	Ashfold et al. 1981
R120	1.66E-18	HCH+OH==>CH+H2O	Jasper et al. 2007
R121	1.25E-10	HCH+OH==>CH2O+H	Jasper et al. 2007
R122	3.00E-11	H2C+C2H3==>CH3+C2H2	Tsang et al. 1986
R123	3.00E-11	H2C+C2H5==>CH3+C2H4	Tsang et al. 1986
R124	7.00E-11	H2C+CH3==>C2H4+H	Tsang et al. 1986
R125	1.00E-28	H2C+CO+A==>CH2CO+A	Yung et al. 1988
R126	3.90E-14	H2C+CO2==>H2CO+CO	Tsang et al. 1986
R127	1.37E-10	H2C+H==>CH+H2	Baulch et al. 1992
R128	1.42E-29	H2C+H+A==>CH3+A	Gladstone et al. 1996
R129	2.00E-10	H2C+O==>CO+H+H	Baulch at al. 1994
R130	8.00E-12	H2C+O==>CH+OH	Huebner et al. 1980
R131	8.30E-11	H2C+O==>CO+H2	Baulch at al. 1994
R132	1.00E-11	H2C+O==>HCO+H	Huebner et al. 1980
R133	3.37E-12	H2C+O2==>HCO+OH	Baulch et al. 1994
R134	1.01E-11	CH2O+OH==>H2O+HCO	Baulch at al. 1994
R135	1.73E-13	CH2O+O==>OH+HCO	Baulch at al. 1994
R136	5.71E-14	CH2O+H==>H2+HCO	Baulch at al. 1994
R137	3.33E-05	N2O==>N2+Od	Pavlov et al. 2001
R138	7.40E-05	NO==>N+O	Pavlov et al. 2001

R139	2.34E-01	NO2==>NO+O	Pavlov et al. 2001
R140	6.84E-02	HNO2==>NO+OH	Pavlov et al. 2001
R141	4.62E-03	HNO3==>NO2+OH	Pavlov et al. 2001
R142	6.84E-02	HNO==>NO+H	Pavlov et al. 2001
R143	1.00E-30	NH3==>NH2+H	Pavlov et al. 2001
R144	3.33E-03	NH==>N+H	Pavlov et al. 2001
R145	3.33E-03	NH2==>NH+H	Pavlov et al. 2001
R146	1.53E-01	NH2==>NHH	Pavlov et al. 2001
R147	6.71E-11	N2O+Od==>NO+NO	DeMore et al., 1997
R148	4.90E-11	N2O+Od==>N2+O2	DeMore et al., 1997
R149	4.94E-34	N2O+H==>NO+NH	Bozzelli et al. 1994
R150	4.31E-18	N2O+H==>OH+N2	Arthru et al. 1997
R151	1.49E-17	N2O+H==>HNNO	Diar et al. 1995
R152	8.02E-19	N2O+OH==>HO2+N2	Tsang et al. 1991
R153	6.88E-31	NO+OH+A==>HNO2+A	DeMore et al. 1997
R154	3.86E-32	NO+H+A==>HNO+A	Tsang et al. 1991
R155	8.93E-32	NO+O+A==>NO2+A	DeMore et al. 1997
R156	5.80E-15	NO+Od==>O2+N	Blais 1985 (upper limit)
R157	8.84E-12	NO+HO2==>NO2+OH	Atkinson et al. 2004
R158	1.35E-11	NO+HCO==>CO+HNO	Dammeier et al., 2007
R159	1.18E-29	NO+CH3+A==>CH3NO+A	Jodkowski et al., 1993
R160	3.65E-12	NO+HCH==>HCN+OH	Fikri et al., 2001
R161	3.65E-11	NO+HCH==>H+HCNO	Fikri et al., 2001
R162	1.37E-10	NO+CH==>O+HCN	Bergeat et a l., 1998
R163	3.99E-11	NO+CH==>H+NCO	Bergeat et a l., 1998
R164	1.33E-11	NO+CH==>HCO+N	Bergeat et a l., 1998
R165	2.00E-10	NO+CH==>CO+NH	Geiger et al., 1999
R166	1.40E-10	NO+CH==>OH+CN	Geiger et al., 1999
R167	1.54E-11	NO+NCO==>CO+N2O	Lin et al. 1993
R168	1.96E-11	NO+NCO==>CO2+N2	Lin et al. 1993
R169	2.16E-15	NH+NH==>NH2+N	Klippenstein et al. 2009

R170	1.44E-28	NH+NH+A==>HNNH+A	Nicholas et al. 1986
R171	1.16E-09	NH+NH==>N2+H+H	Meaburn et al. 1968
R172	3.67E-19	NH+NO==>O+HNN	Bozzelli et al. 1994
R173	2.87E-11	NH+NO==>N2O+H	Bozzelli et al. 1994
R174	4.78E-12	NH+NO==>OH+N2	Bozzelli et al. 1994
R175	1.17E-20	NH+OH==>NH2+O	Cohen et al. 1991
R176	6.81E-11	NH+OH==>H+HNO	Klippenstein et al. 2009
R177	1.39E-12	NH+OH==>H2O+N	Klippenstein et al. 2009
R178	1.89E-11	NH+N==>N2+H	Caridade et al. 2005
R179	1.16E-10	NH+O==>NO+H	Cohen et al. 1991
R180	1.16E-11	NH+O==>OH+N	Cohen et al. 1991
R181	2.11E-24	NH+CH4==>CH3+NH2	Xu et al. 1999
R182	1.25E-32	N+N+A==>N2+A	Knipovich et al. 1988
R183	9.16E-33	N+O+A==>NO+A	Campbell et al. 1973
R184	1.89E-11	N+NH==>N2+H	Caridade et al. 2005
R185	5.02E-32	N+H+A==>NH+A	Brown et al. 1973
R186	2.92E-11	N+NO==>N2+O	DeMore et al. 1997
R187	4.70E-11	N+OH==>NO+H	Baulch et al. 1994
R188	1.66E-10	N+CH==>CN+H	Brownsword et al. 1996
R189	1.00E-05	N+CH3==>H2NC+H	Cimas et al. 2006
R190	1.00E-36	N+H2+A==>NH2+A	Petrishchev et al. 1981
R191	2.69E-34	N+CH4+A==>CH3NH+A	Aleksandrov et al. 1989
R192	2.51E-14	N+CH4==>HCN+H2+H	Takahashi 1972
R193	7.47E-11	NH2+O==>H+HNO	Cohen et al. 1991
R194	1.16E-11	NH2+O==>OH+NH	Cohen et al. 1991
R195	8.30E-12	NH2+O==>H2+NO	Cohen et al. 1991
R196	1.65E-14	NH2+NH==>NH3+N	Klippenstein et al. 2009
R197	1.70E-10	NH2+NH==>HNNH+H	Klippenstein et al. 2009
R198	2.06E-15	NH2+NH2==>NH3+NH	Klippenstein et al. 2009
R199	1.42E-29	HN2+H+A==>NH3+A	Altinay et al. 2012

R200	3.59E-12	HNO+NH2==>NH3+NO	Xu et al. 2009
R201	2.38E-14	HNO+NH2==>H+NH2NO	Xu et al. 2009
R202	3.84E-17	HNO+NH2==>NH2NHO	Xu et al. 2009
R203	4.54E-18	NH2+H2==>NH3+H	Mebel et al. 1999
R204	1.24E-11	NH2+NO==>N2+H2O	Park et al. 1999
R205	1.37E-12	NH2+NO==>OH+HNN	Park et al. 1999
R206	1.72E-15	NH2+NH2OH==>NH3+NHOH	Klippenstein et al. 2009
R207	2.55E-14	NH2+NH2OH==>NH3+NH2O	Klippenstein et al. 2009
R208	1.10E-21	NH2+H2O==>OH+NH3	Cohen et al. 1991
R209	3.19E-12	NH2+HNNH==>NH3+HNN	Linder et al. 1996
R210	3.93E-24	NH2+OH==>H+NH2O	Mousavipour et al. 2009
R211	3.92E-13	NH2+OH==>H2O+NH	Mousavipour et al. 2009
R212	2.21E-33	NH2+OH==>H2+HNO	Mousavipour et al. 2009
R213	1.32E-36	NH2+OH==>H2+NOH	Mousavipour et al. 2009
R214	8.01E-14	NH2+OH==>NH3+O	Mousavipour et al. 2009
R215	3.93E-24	NH2+OH==>H+NH2O	Mousavipour et al. 2009
R216	1.75E-27	CH3+NH2+A==>CH3NH2+A	Jodkowski et al. 1995
R217	8.40E-17	CH3+NH2==>CH4+NH	Xu et al. 1999
R218	8.63E-19	C2H5+NH2==>C2H6+NH	Xu et al. 1999
R219	3.98E-21	CH4+NH2==>CH3+NH3	Song et al. 2003
R220	3.51E-16	HO2+NH2==>H2O+NOH	Sumathi et al. 1996
R221	2.50E-16	HO2+NH2==>H2O+HNO	Sumathi et al. 1998
R222	6.33E-18	HO2+NH2==>NH3+O2	Sumathi et al. 1996
R223	3.19E-11	HO2+NH2==>OH+NH2O	Sumathi et al. 1996
R224	5.25E-17	NH2+CH2O==>NH3+HCO	Li et al. 2002

R225	5.85E-18	HCN+O==>CO+NH	Perry et al. 1985
R226	4.99E-18	HCN+O==>H+NCO	Perry et al. 1985
R227	1.70E-30	HCN+O==>CN+OH	Perry et al. 1985
R228	4.72E-28	HCN+H==>CN+H2	Tsang et al. 1991
R229	4.28E-19	HCN+OH==>CN+H2O	Tsang et al. 1991
R230	3.18E-22	HCN+OH==>CO+NH2	Miller et al. 1988
R231	1.23E-36	HCN+HCO==>CH2O+CN	Feng et al. 1997
R232	1.40E-10	CN+O==>CO+N	Andersson et al. 2003
R233	1.66E-12	HNNO+OH==>NO+NHOH	Lin et al. 1992
R234	2.90E-14	HNNO+NO==>N2+HNO2	Lin et al. 1992
R235	2.16E-12	HNNO+NO==>NO2+HNN	Lin et al. 1992
R236	3.57E-14	HNO+NO2==>HNO2+NO	Tsang et al. 1991
R237	1.04E-11	HNO+CH3==>CH4+NO	Choi et al. 2005
R238	3.20E-30	NO2+OH+A==>HNO3+A	Troe 2012
R239	3.63E-13	HNO3+NH2==>NH3+NO3	Xu et al. 2010
R240	3.20E-30	NO2+OH+A==>HNO3+A	Troe 2012
R241	4.09E-16	NO2+OH==>HO2+NO	Tsang et al. 1991
R242	1.45E-10	NO2+CH==>HCO+NO	Tao et al. 2001
R243	1.70E-11	NO3+O==>NO2+O2	Atkinson et al. 2004
R244	2.59E-11	NO3+NO==>NO2+NO2	Atkinson et al. 2004
R245	2.00E-11	NO3+OH==>NO2+HO2	Atkinson et al. 2004
R246	2.51E-10	NH3+Od==>OH+NH2	DeMore et al. 1997
R247	1.18E-24	NH3+CH3==>CH4+NH2	Yu et al. 1998
R248	1.58E-31	N2+CH==>CHN2	Le Picard et al. 1998
R249	1.58E-31	N2+CH==>CHN2	Le Picard et al. 1998
R250	3.32E-11	HO2+NCO==>HNCO+O2	He et al. 1993
R251	5.70E-11	HO2+O==>OH+O2	Atkinson et al. 2004
R252	5.70E-11	HO2+O==>OH+O2	Atkinson et al. 2004
R253	5.33E-80	HO2+NO==>HOONO	Zhu et al. 2003
R254	1.11E-14	HO2+NO==>O2+HNO	Howard 1979

R255	8.86E-12	HO2+NO==>OH+NO2	Atkinson et al.2004
R256	5.87E-35	HO2+H2O==>OH+H2O2	Lloyd 1974
R257	3.80E-11	HNO+O==>OH+NO	Inomata 1999
R258	3.02E-19	HNO+HNO==>NO+NHOH	Lin et al. 1992
R259	8.48E-18	HNO+HNO==>N2O+H2O	Lin et al. 1992
R260	1.12E-14	HNO+NHOH==>NH2OH+NO	Lin et al. 1992
R261	2.14E-22	HNO+H==>NH+OH	Cohen et al. 1991
R262	5.68E-12	HNO+H==>H2+NO	Tsang et al. 1991
R263	1.51E-11	HNO+OH==>H2O+NO	Tsang et al. 1991
R264	3.81E-19	HNO+CH3==>CH3NO+H	Choi et al. 2005
R265	4.49E-29	HNO+HCO==>CO+NHOH	Xu et al. 2004
R266	4.47E-24	HNO+HCO==>CO+NH2O	Xu et al. 2004
R267	8.19E-25	HNO+HCO==>CH2O+NO	Xu et al. 2004
R268	5.25E-11	HNO+CH3O==>CH3OH+NO	He et al. 1988
R269	7.49E-14	NH2OH+OH==>H2O+NHOH	Klippenstein et al. 2009
R270	4.66E-15	NH2OH+OH==>H2O+NH2O	Klippenstein et al. 2009
R271	1.66E-12	NHOH+H==>H2+HNO	Lin et al. 1992
R272	1.66E-12	NHOH+OH==>H2O+HNO	Lin et al. 1992
R273	1.52E-05	NHOH+HCO==>CO+NH2OH	Xu et al. 2004
R274	1.85E-08	NHOH+HCO==>CO+H2+HNO	Xu et al. 2004
R275	1.64E-05	NHOH+HCO==>CH2O+HNO	Xu et al. 2005
R276	1.99E-11	HNO2+O==>OH+NO2	Tsang et al. 1991
R277	6.43E-13	HNO2+H==>H2O+NO	Hsu et al. 1997
R278	1.26E-11	HNO2+H==>OH+HNO	Hsu et al. 1997
R279	2.27E-12	HNO2+H==>H2+NO2	Hsu et al. 1997
R280	6.00E-12	HNO2+OH==>H2O+NO2	Atkinson et al. 2004
R281	3.23E-32	HNO2+HCO==>CO+H2O+NO	Xu et al. 2004
R282	1.43E-51	HNO2+HCO==>CH2O+NO2	Xu et al. 2004
R283	3.63E-13	HNO3+NH2==>NH3+NO3	Xu et al. 2010
R284	3.76E-19	HNO3+H==>H2O+NO2	Boughton et al. 1997

R285	6.41E-24	HNO3+H==>H2+NO3	Boughton et al. 1997
R286	1.50E-20	HNO3+NO==>HNO2+NO2	Kaiser et al. 1977
R287	4.18E-11	CN+NCO==>CO+NCN	Tzeng et al. 2009
R288	1.69E-11	CN+O==>CO+N	Baulch et al. 1992
R289	8.05E-11	CN+NO2==>NO+NCO	Park et al. 1993
R290	7.11E-12	CN+NO2==>CO+N2O	Park et al. 1993
R291	5.20E-12	CN+NO2==>CO2+N2	Park et al. 1993
R292	1.60E-13	CN+NO==>CO+N2	Li et al. 1985
R293	2.42E-11	CN+O2==>O+NCO	Baulch et al. 1994
R294	1.66E-16	CN+NH3==>HCN+NH2	Baulch et al. 1981
R295	2.47E-14	CN+H2==>HCN+H	Choi et al. 2004
R296	8.58E-13	CN+CH4==>HCN+CH3	Baulch et al. 1994
R297	1.69E-13	CN+CH2O==>CN+HCO	Feng et al. 1997