Kinetic study of abiotic amino acid formation by UV-irradiation

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Received 2 December 2002; received in revised form 14 February 2003; accepted 26 August 2003

Abstract

Glycine was produced in a solution of 2-aminoethanol, methylamine, ethylamine, or acetonitrile by UV-irradiation. The concentrations of the reactants and glycine were analyzed under six different conditions. Each reaction was assumed to be a first-order reaction. Then, the rate constant of the degradation of the reactants, and also those of the formation and degradation of glycine were calculated. Each rate constant of the glycine degradation was at least 10 times larger than that of the glycine formation. Glycine did not accumulate but instead disappeared on prolonged UV-irradiation when the reactants were supplied to the environment only once at initiation of the irradiation. Furthermore, the concentrations of glycine under six different conditions were calculated using the determined rate constants when the reactants were supplied continuously to the model environment. Glycine concentrations did not continue to increase with an increase in the duration of irradiation. The maximum concentration of glycine was determined by the rate constant of the degradation of the reactant, and also by the rate constants of the formation and degradation of glycine. Therefore, determination of the rate constants was shown to be important for considering the prolonged phenomenon of chemical evolution.

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Keywords: Amino acid; UV-irradiation; Abiotic formation; Kinetics

1. Introduction

The formation of amino acids using various energy sources has been widely studied (e.g., electric discharge (Miller, 1953; Wolman et al., 1972; Harada and Iwasaki, 1974), β-irradiation (Hasselstrom et al., 1957), electron irradiation (Palm and Calvin, 1962; Oro, 1963), heating (Harada and Fox, 1964; Yoshino et al., 1971; Marshall, 1994), flame oxidation (Nomoto et al., 1983, 1996; Terasaki et al., 2002a), arc plasma (Harada et al., 1984). UV-light is one of the most efficient and common energy sources for the abiotic synthesis of organic compounds on the primitive earth (Chyba and Sagan, 1992) and interstellar media (Hagen et al., 1979; Prasad and Trafadar, 1983). Many studies of the abiotic synthesis of amino acids by UV-irradiation have been reported (e.g., Bahadur, 1954; Deschreider, 1958; Bar-Nun and Chang, 1983; Kihara et al., 1991; Bernstein et al., 2002; Munoz Caro et al., 2002; Takano et al., 2002; Terasaki et al., 2002b). In most of those studies, the amino acid products were identified and quantified at a certain fixed duration of irradiation. In some cases, the ratio of the amino acid generation efficiency to the amount of the irradiation energy [quantum yield (Munoz Caro et al., 2002), G value (Takano et al., 2002)] and the formation rates of products (Robertson and Miller, 1995) are discussed in order to compare the effects of a variety of reaction conditions, and also to compare the efficacy of various sources of amino acids. Nevertheless, it does not suffice to study the prolongation phenomenon of chemical evolution alone, but rather it is necessary to include an analysis of the rate at which the degradation reactions of amino acids occur.

In this report, we showed time courses of concentrations of glycine, which was the most abundant amino acid product in the UV-irradiation experiments. Although glycine accumulated in the initial stage of the reaction, amounts of glycine degradation exceeded that of glycine formation with decreasing reactant concentrations. Finally, all of the produced glycine

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decomposed and disappeared. Then, we determined the rate constants of the glycine formation; in addition, we considered the rate constants of degradation of reactants and glycine. Furthermore, the time courses of glycine concentrations were calculated when the reactants were supplied to the model environment continuously, and compared with the time courses of glycine concentration in the batch reaction in order to demonstrate the usefulness of the determination of the rate constants of the reactant degradation, and amino acids formation and degradation.

2-Aminoethanol, methylamine, ethylamine and acetonitrile were used as the reactants. Methylamine was detected in the Murchison meteorite (Pizzarello et al., 1994), and in the interstellar media (Kaifu et al., 1974). Ethylamine was detected in the Murchison meteorite (Pizzarello et al., 1994) and was used as a source for glycine formation by UV-irradiation (Munegumi et al., 1990). Acetonitrile was detected in the Orion KL region (Wright et al., 1996) and in the comet Hale-Bopp (Bockelee-Morvan et al., 2000). Acetonitrile was reported as a source for glycine formation by ionizing radiation (Draganic et al., 1977). 2-Aminoethanol was an important intermediate from ethylamine to glycine by UV-irradiation (Munegumi et al., 1990).

2. Experiments

The UV-irradiation experiments were performed using the apparatus shown in Fig. 1. A low-pressure mercury lamp (Riko Kagaku Sangyo, UVL-32) was used as the UV-light source, the $\lambda_{max}$ of which was 254 nm and the flux of which was approximately $6 \times 10^{15}$ photon cm$^{-2}$ s$^{-1}$, as determined by a chemical actinometer used with potassium ferrioxalate (Hatchard and Parker, 1956). This flux was nearly 100 times higher than that at the upper atmosphere of the primitive earth (Chyba and Sagan, 1992). Approximately 300 ml of the reaction solution was poured into the reaction vessel. The UV lamp, covered in quartz, was immersed into the reaction solution. The atmosphere was replaced with argon to remove oxygen in the reaction vessel. The reaction temperature was maintained by a water bath. At regular time intervals, approximately 10-ml aliquots of the reaction solution were sampled. The concentrations of glycine and amines were analyzed by an amino acid analyzer (JEOL, JLC-300) without hydrolysis. The acetonitrile concentration was determined by gas chromatography using a Gaskuropack 54 80/100 packed column (2 m × 3 mm i.d., GL Science). The concentrations of the reactants, pH, and reaction temperature are shown in Table 1.

### Table 1: Reaction conditions

<table>
<thead>
<tr>
<th>Run</th>
<th>Reactant</th>
<th>Concentration (mol l$^{-1}$)</th>
<th>pH</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-Aminoethanol</td>
<td>$2.38 \times 10^{-3}$</td>
<td>10</td>
<td>293</td>
</tr>
<tr>
<td>2</td>
<td>Methylamine</td>
<td>$9.65 \times 10^{-3}$</td>
<td>10</td>
<td>293</td>
</tr>
<tr>
<td>3</td>
<td>Methylamine</td>
<td>$1.19 \times 10^{-2}$</td>
<td>2</td>
<td>293</td>
</tr>
<tr>
<td>4</td>
<td>Ethylamine</td>
<td>$1.03 \times 10^{-2}$</td>
<td>10</td>
<td>293</td>
</tr>
<tr>
<td>5</td>
<td>Ethylamine</td>
<td>$1.05 \times 10^{-2}$</td>
<td>2</td>
<td>293</td>
</tr>
<tr>
<td>6</td>
<td>Acetonitrile</td>
<td>$1.09 \times 10^{-3}$</td>
<td>ca. 7</td>
<td>273</td>
</tr>
</tbody>
</table>

*Solution pH was adjusted with HCl or NaOH.
**Without adjustment.

3. Results and discussion

3.1. Determining the rate constants

The concentrations of 2-aminooethanol and glycine in the UV-irradiated 2-aminooethanol solution are shown in Fig. 2. The degradation mechanism of 2-aminooethanol and glycine was not clear, but was considered to be an intermolecular dissociation by photoexcitation and/or a reaction with hydroxy and hydrogen radicals produced by the photodissociation of water. The concentrations of hydroxy and hydrogen radicals were almost constant throughout the reaction due to excess amounts of water. The degradation reactions were, therefore, considered as first-order reactions. Glycine formation from 2-aminooethanol was an oxidation reaction with a hydroxy radical, which was the dissociation product of water by UV-irradiation (Munegumi et al., 1990). Apparently, it is possible that the formation of glycine was a first-order reaction, because the concentration of the hydroxy radical is almost constant. Thus, the degradation rate of the reactant can be described as follows:

\[
\frac{d[S]}{dt} = -k[S], \quad [S]_{t=0} = C,
\]

Fig. 1. Schematic drawing of the apparatus used for the UV-irradiation experiment. (a) Low-pressure mercury lamp; (b) quartz cover; (c) reaction solution; (d) reaction vessel; (e) water bath; (g) condenser; (f) argon gas inlet.
where \([S]\) is the concentration of the reactant at time \(t\), \(k_s\) is the rate constant of the reactant degradation, and \(C\) is the initial concentration of reactant. Thus,

\[
[S] = Ce^{-k_s t}.
\] (2)

Experimental data were fitted to Eq. (2) with the Levenberg–Marquardt algorithm (More, 1977) on a Kaleida Graph (Synergy Software), and \(k_s\) was determined to be \(6.00 \times 10^{-4}\) s\(^{-1}\). The regression curve is shown in Fig. 2(a) and reflects the experimental data well. In this experiment, 2-aminoethanol rapidly degraded, and disappeared altogether within 2.5 h.

Then, the formation rate of glycine was defined as

\[
\frac{d\text{[Gly]}}{dt} = k_f [S] - k_d \text{[Gly]}, \quad \text{[Gly]}_{t=0} = 0,
\] (3)

where \([\text{Gly}]\) is the glycine concentration at time \(t\), \(k_f\) is a formation rate constant of glycine, and \(k_d\) is a degradation rate constant of glycine, such that

\[
\text{[Gly]} = C \frac{k_f}{k_s + k_d} (e^{-k_s t} - e^{-k_d t}).
\] (4)

The experimental data were fitted to Eq. (4), as was done in the calculation described above; \(k_f\) and \(k_d\) were determined as being \(1.38 \times 10^{-5}\) s\(^{-1}\) and \(1.25 \times 10^{-4}\) s\(^{-1}\), respectively. In this calculation, the above result was used for the \(k_s\). The regression curve is shown in Fig. 2(b) and did not have as good of a fit, as was the case with the results of the time course of 2-aminoethanol. However, the outline of the glycine concentration as affected by UV-irradiation was expressed with Eq. (4). In this case, the degradation rate constant of glycine was nearly 10 times larger than the rate constant of glycine formation. The maximum yield of glycine was approximately 1.5% of the reactants at 1 h, according to the present calculations.

The concentrations of the reactants and glycine in the solution of methylamine, ethylamine, and acetonitrile by the UV-irradiation are shown in Fig. 3. Each reaction was assumed to follow a first-order kinetics, and the rate constants of the degradation of reactants, and the rate constants of the formation and degradation of glycine were determined using the same procedures as those described above. Each reaction rate constant is shown in Table 2. Regression curves are also shown in Fig. 3. Degradations of reactants and glycine were considered as first-order reactions, as was the case using 2-aminoethanol. Each regression curve of the concentrations of the reactants was reflected sufficiently in the experimental data (Fig. 3(a), (c) and (e)). The formation mechanism of glycine from ethylamine in acidic conditions was reported by Munegumi et al. (1990) and was a multi-step oxidation by hydroxy radicals. However, it remains unclear which step was the rate-determining step. Since the formation of diaminomaleonitrile was reported in the case of UV-irradiation of acetonitrile (Okuyama and Nishi, 1984), it was concluded that amino acid formation from acetonitrile could be similar to the Strecker-type synthesis. Amino acid formation from methylamine was not clearly demonstrated. The dissociation of methylamine to the methyl radical would be an important step for the glycine formation in the methylamine solution. In addition, rate constants of glycine degradation were different by each experiment (Table 2). This is because different radical species in different concentrations existed as by-products and/or intermediates in the reaction solution. It was reported that the major product was changed by the different concentrations of the intermediate radicals from the different concentrations of reactant (Nomoto et al., 1991). It was, in any case, difficult to conclude theoretically that formation reactions of glycine were first-order reactions. However, the regression curves of glycine concentrations were in good agreement with the experimental data (Fig. 3(b), (d) and (f)). As a result, it was concluded that these reactions were pseudo-first-order reactions. The determined rate constants were used for the following calculations.
3.2. Calculating in a model environment

When the reactants were continuously supplied to the model environment at the same concentration \( C \text{ mol l}^{-1} \text{ s}^{-1} \), the degradation rate of the reactants can be defined as follows:

\[
\frac{d[S]}{dt} = -k_s[S] + C, \quad [S]_{t=0} = 0,
\]

thus,

\[
[S] = C \frac{1 - e^{-k_s t}}{k_s}.
\]

Then, the glycine concentration at time \( t \) was calculated with Eqs. (3) and (6),

\[
[Gly] = C \frac{k_i}{k_b k_d} \frac{(1 - e^{-k_d t}) k_b + (1 - e^{-k_i t}) k_d}{-k_i + k_d},
\]

The time courses of acetonitrile and glycine in the acetonitrile solution by UV-irradiation are shown in Fig. 4, using the determined rate constants given in Table 2.
the data of the UV-flux at the upper atmosphere of the primitive earth (Chyba and Sagan, 1992).

The maximum concentrations of glycine produced by UV-irradiation were calculated as follows:

\[
\lim_{t \to \infty} [\text{Gly}] = C \frac{k_e}{k_f k_d}.
\]  

(8)

The maximum concentrations of glycine and the times at maximum concentration were calculated and are shown in Table 3. One of the two following conditions applied: the reactants were either supplied continuously with \( C \) mol \( l^{-1} s^{-1} \) or only once at initiation with \( C \) mol \( l^{-1} \). When the reactants were supplied once at initiation, the highest glycine yield was attained by the reaction from 2-aminoethanol at pH 10 among our six conditions. In this case, the rate constant of glycine formation was the largest among the six conditions, even if that of glycine degradation was also large. This is an effective condition for obtaining large quantities of glycine in batch experiments of short duration. However, glycine from ethylamine at pH 2 was the most effective condition among six experiments, when the reactants were supplied to the model environment continuously. In this case, the rate constants of glycine degradation and reactant degradation were the smallest among the six conditions, even if that of glycine formation rate constant was small. Furthermore, it took the longest irradiation time that the concentration of glycine was achieved at maximum.

The best condition of glycine accumulation in the continuous reactant-supply system does not reflect the result of glycine concentration at the fixed time in the batch reaction. The maximum concentration of glycine when the reactants supplies to the model environment continuously, is determined by the reactant concentration in the experiment \((C/k_d)\) and the ratio of formation of glycine to degradation of glycine \( (k_f/k_d)\) according to Eq. (8). Therefore, determining the rate constants of reactant degradation, product formation and product degradation is important for considering the prolonged phenomenon of chemical evolution. The importance of determination of the three rate constants is not only

Table 2
Rate constants in the UV-irradiation experiments

<table>
<thead>
<tr>
<th>Run</th>
<th>Reactant</th>
<th>Rate constant ((s^{-1}))</th>
<th>Degradation ((k_d))</th>
<th>Formation ((k_f))</th>
<th>Degradation ((k_d))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-Aminoethanol</td>
<td>(6.00 \times 10^{-4})</td>
<td>(1.38 \times 10^{-5})</td>
<td>(1.25 \times 10^{-4})</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Methylamine</td>
<td>(2.07 \times 10^{-5})</td>
<td>(1.52 \times 10^{-8})</td>
<td>(9.91 \times 10^{-6})</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Methylamine</td>
<td>(8.98 \times 10^{-6})</td>
<td>(9.14 \times 10^{-9})</td>
<td>(3.91 \times 10^{-6})</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ethylamine</td>
<td>(4.15 \times 10^{-5})</td>
<td>(6.03 \times 10^{-10})</td>
<td>(1.65 \times 10^{-6})</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Ethylamine</td>
<td>(9.88 \times 10^{-6})</td>
<td>(5.49 \times 10^{-8})</td>
<td>(1.94 \times 10^{-7})</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Acetonitrile</td>
<td>(5.05 \times 10^{-5})</td>
<td>(1.11 \times 10^{-6})</td>
<td>(7.58 \times 10^{-4})</td>
<td></td>
</tr>
</tbody>
</table>

Table 3
Maximum concentrations of glycine in the model environments

<table>
<thead>
<tr>
<th>Run</th>
<th>Reactant</th>
<th>Maximum at initiation* ((\text{mol} l^{-1}))</th>
<th>Time (h)</th>
<th>Maximum** ((\text{mol} l^{-1}))</th>
<th>Time*** (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-Aminoethanol</td>
<td>(1.5 \times 10^{-2} \times C)</td>
<td>0.92</td>
<td>(1.8 \times 10^{2} \times C)</td>
<td>(&gt;15.9)</td>
</tr>
<tr>
<td>2</td>
<td>Methylamine</td>
<td>(3.7 \times 10^{-4} \times C)</td>
<td>19.0</td>
<td>(7.4 \times 10 \times C)</td>
<td>(&gt;212)</td>
</tr>
<tr>
<td>3</td>
<td>Methylamine</td>
<td>(5.4 \times 10^{-4} \times C)</td>
<td>45.6</td>
<td>(2.6 \times 10^{2} \times C)</td>
<td>(&gt;531)</td>
</tr>
<tr>
<td>4</td>
<td>Ethylamine</td>
<td>(1.3 \times 10^{-3} \times C)</td>
<td>22.5</td>
<td>(8.8 \times C)</td>
<td>(&gt;1170)</td>
</tr>
<tr>
<td>5</td>
<td>Ethylamine</td>
<td>(5.1 \times 10^{-3} \times C)</td>
<td>112</td>
<td>(2.8 \times 10^{2} \times C)</td>
<td>(&gt;9920)</td>
</tr>
<tr>
<td>6</td>
<td>Acetonitrile</td>
<td>(1.2 \times 10^{-3} \times C)</td>
<td>1.06</td>
<td>(2.9 \times 10 \times C)</td>
<td>(&gt;38.4)</td>
</tr>
</tbody>
</table>

* Initial concentration of reactant was \( C \) mol \( l^{-1} \).

** Reactant equivalent to \( C \) mol \( l^{-1} s^{-1} \) was supplied to the model environment, continuously.

*** Time at 99.9% of maximum accumulation.
applicable for UV-irradiation reactions, but also for the reactions using with other energy sources (e.g., electric discharge, β-irradiation, electron irradiation, heating, flame oxidation, arc plasma).

4. Conclusions

Glycine was produced in UV-irradiation experiments from 2-aminoethanol, methylamine, ethylamine, or acetonitrile. Each reaction was assumed to be a first-order reaction, and the rate constants of the degradation of the reactants, and of the formation and degradation of glycine were calculated under the six above mentioned conditions. It was difficult to demonstrate theoretically that these reactions were first-order reactions. However, the outlines of glycine concentration in the UV-irradiation experiments were expressed by the equations of the first-order reaction.

The concentrations of glycine were calculated using the determined rate constants, whereby the reactants were continuously supplied to the model environment. However, even when the reactants were supplied continuously, the accumulation of glycine stopped when the reactant concentrations achieved equilibrium. Effective conditions in the batch reaction and in the continuous reactant-supply system were different. By determining the rate constants of the degradation of the reactants, as well as the rate constants of the formation and degradation of the produced amino acid, it became possible to estimate the amount of amino acid accumulation under various conditions.

Acknowledgements

We thank two referees for helpful comments. The amino acid analyzer was used at the Chemical Analyses Center of the University of Tsukuba with the assistance of Mr. H. Nakazono. This study was partially supported by the University of Tsukuba Research Project, 2001 and the Inoue Foundation for Science, Tokyo.

References


