

# CONSTANT AMP SYNTHESIS IN AQUEOUS SOLUTION BY ELECTRIC DISCHARGES

Y. YAMAGATA, T. MOHRI, M. YAMAKOSHI, and K. INOMATA

*Department of Physics and Department of Chemistry, Faculty of Science, Kanazawa University, Marunouchi, Kanazawa 920, Japan*

(Received 2 September, 1980)

**Abstract.** An electric discharge was made through a gas mixture of N<sub>2</sub> (7 cm Hg), H<sub>2</sub> (14 cm Hg) and CO<sub>2</sub> (14 cm Hg) over an aqueous solution (100 ml, pH 7.6) of adenosine (0.02 M) and phosphate (0.2 M) in a 5 liter vessel simulating primitive earth conditions. AMP was produced at a constant rate in the solution, and the yield reached about 2% in two months.

Various experiments have been performed concerning dehydration condensation under simulated prebiotic conditions to study chemical evolution (Calvin, 1969; Miller and Orgel, 1974; Ponnampertuma, 1978). However, there has never been an experiment where dehydration condensation could be continued in a closed system simulating the primitive Earth, if energy were supplied continuously in a special form from the exterior of the system.

Recently we have constructed a new type of discharge apparatus to simulate prebiotic chemical evolution, and we reported that AMP and pyrophosphate were produced by electric discharge through a model primitive gas mixture placed over a solution using the apparatus (Yamagata *et al.*, 1979). The results have shown a strong dependence of the yield of AMP on the starting conditions. For the experiment which resulted in the highest yield of AMP after a week of discharge, the discharge was further continued over a period of about a month to investigate the dependence of the yield on the discharge time. The yield increased initially and then reached a maximum (about 0.5%) after about two weeks, and then decreased rapidly (filled circles in Figure 1). The pattern of the change was parallel to that of the pH of the solution. These results suggested that the decrease of the yield is due to the decomposition of adenosine by oxidants such as nitric acid produced by electric discharge from the remaining gases which changed gradually toward oxidative compositions. We have continued experiments to find the starting conditions in which dehydration condensation proceeded constantly during the discharge. We now report that such conditions have been obtained by a modification of the starting condition of the solution of run 8 in the previous report (Yamagata *et al.*, 1979).

The experiments were carried out with the same apparatus and procedures described in the previous report (Yamagata *et al.*, 1979) except that seven parallel discharges were made between the center electrode and the surrounding seven electrodes. The starting gas contained nitrogen (7 cm Hg), hydrogen (14 cm Hg) and carbondioxide (14 cm Hg), the same as run 8 of the previous report (Yamagata *et al.*,

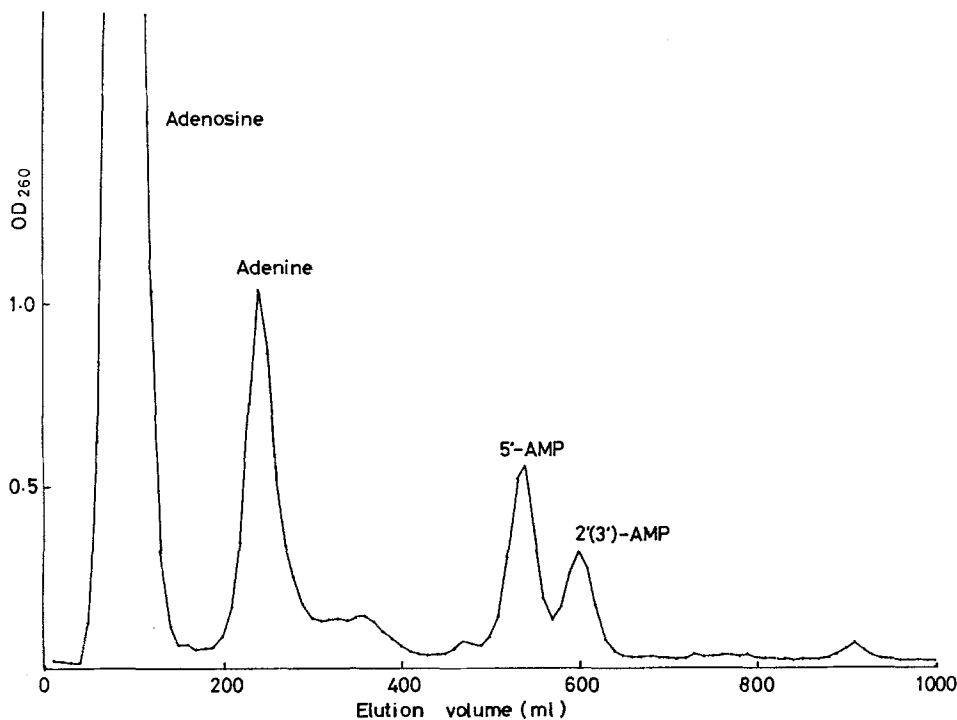


Fig. 1. DEAE-Sephadex A-25 column chromatogram illustrating AMP production (Sample; 5 ml of the final solution). 5'-AMP and 2'(3')-AMP were identified on silica gel TLC. 2'(3')-AMP was separated into two nearly equal UV-absorbing spots corresponding to 2'- and 3'-AMP on cellulose TLC as in the previous result (Yamagata *et al.*, 1979).

1979), but the pH of the starting solution was modified. 100 ml of the solution of 0.02 M adenosine and 0.2 M phosphate (0.4 g  $\text{KH}_2\text{PO}_4$  + 3.0 g  $\text{K}_2\text{HPO}_4$ ) was prepared to be weakly basic (pH 7.6).

Figure 1 shows a typical ion exchange chromatogram on a DEAE-Sephadex column indicating the production of AMP. The experimental results are shown in Figure 2 together with those of run 8 of the previous report. The yield of AMP increased linearly with the duration of discharge except for the last period, and it reached about 2% after two months of discharge. The change of pH of the solution during the discharge diminished compared to that of the previous experiment, and pH was almost constant. This is due not only to the buffering action of the present solution, but also to the decrease of the absorbing capacity of the solution for ammonia produced by the discharge. The concentration of ammonia (or ammonium ion) of the final solution was estimated to be 0.17 M by titration of dilute sulfuric acid, which absorbed ammonia generated by the addition of sodiumhydroxide.

The slower capture of ammonia by the aqueous phase should result in slower decrease of the pressure and slower increase of the ratio of partial pressure of  $\text{CO}_2$  and  $\text{CO}$ , as ammonia is a reducing substance. This was confirmed by a pressure gauge and gas chromatography. For example, after 2 weeks of discharge the pressure de-

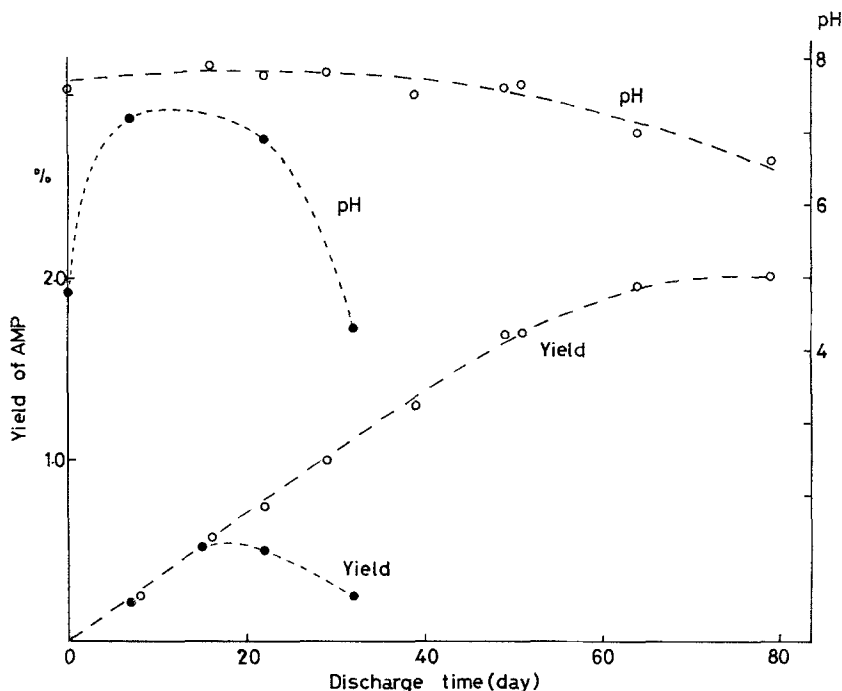


Fig. 2. Dependence of total yield of AMP and pH of the solution on the discharge time (open circles). The previous results (Yamagata *et al.*, 1979) are given for comparison (filled circles).

creased to 20 cm Hg in the previous experiment whereas it decreased only to 25 cm Hg in the present case, and  $P_{CO_2}/P_{CO}$  was about 2 and 0.5 respectively. Urea was also detected in the solution at a concentration of 0.13 M, which was estimated by the amount of ammonia produced upon addition of urease. The production of urea, which changes the gas composition toward a more oxidative state, would depend on the concentration of ammonia.

The slow down of AMP synthesis at the end of the discharge in Figure 2 may be prevented if urea is decomposed to gaseous components or if additional gases are supplied. This compensation of gases must have occurred on the primitive Earth, because of the very short lifetime of urea (Miller and Orgel, 1974) relative to the geological time and because of the continuous degassing from the interior of the Earth.

The fact that the condensation experiment was much improved by using the weakly basic starting solution is interesting from the viewpoint that primitive seawater would have been weakly basic as well as in the present one (Miller and Orgel, 1974).

### References

- Calvin, M.: 1969, *Chemical Evolution*, Oxford University Press, New York.  
 Miller, S. L. and Orgel, L. E.: 1974, *The Origin of Life on the Earth*. Prentice-Hall, Englewood Cliffs.  
 Ponnampuruma, C.: 1978, in H. Noda (ed.), *Origin of Life*, Proceedings of the 2nd ISSOL Meeting, Japan Scientific Societies Press, p. 67.  
 Yamagata, Y., Matsukawa, T., Mohri, T., and Inomata, K.: 1979, *Nature* **282**, 284.