우주와 생명 제 10강

화학적 진화

SEOUL NATIONAL UNIVERSITY

Science 117, 528–529, 1953

가능한 태초 지구 조건에서의 아미노산 생성
A Production Of Amino Acids Under Possible Primitive Earth Conditions

밀러
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INTRODUCTION

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ties of the compounds manometrically (*5*). In the other, the material is applied to the paper along 8 cm of the base line rather than as a spot and, after resolution, areas 8 × 5 cm containing the various compounds are cut from the paper and rolled in shell vials. Ten anesthetized houseflies are then introduced into each vial, and the toxicity of the compounds is characterized by rate of knockdown and 24-hr mortality.

The paper chromatographic method is useful in studying the metabolism of phosphorus insecticides in plants, mammals, and insects. With it, for example, we have been able to demonstrate the conversion of parathion and its methyl analog to the corresponding phosphates by an enzyme system found in *Periplaneta americana* (L.) (*2*). Further studies are in progress. The method has also been of value in studying the action of heat on purified parathion and methyl parathion and in isolating the compounds formed and in studying their biological properties (*1*).

References

1. METCALF, R. L., and MARCH, R. B. To be published.
2. ———. *Ann. Entomol. Soc. Amer.* (in press).
3. KRITCHEVSKY, T. H., and TISELIUS, A. *Science*, **114**, 299 (1951).
4. HANES, C. S., and ISHERWOOD, F. A. *Nature*, **164**, 1107 (1949).
5. METCALF, R. L., and MARCH, R. B. *J. Econ. Entomol.*, **42**, 721 (1949).

Manuscript received September 15, 1952.

A Production of Amino Acids Under Possible Primitive Earth Conditions

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The idea that the organic compounds that serve as the basis of life were formed when the earth had an atmosphere of methane, ammonia, water, and hydrogen instead of carbon dioxide, nitrogen, oxygen, and water was suggested by Oparin (*1*) and has been given emphasis recently by Urey (*2*) and Bernal (*3*).

In order to test this hypothesis, an apparatus was built to circulate CH_4, NH_3, H_2O, and H_2 past an electric discharge. The resulting mixture has been tested for amino acids by paper chromatography. Electrical discharge was used to form free radicals instead of ultraviolet light, because quartz absorbs wavelengths short enough to cause photo-dissociation of the gases. Electrical discharge may have played a significant role in the formation of compounds in the primitive atmosphere.

The apparatus used is shown in Fig. 1. Water is boiled in the flask, mixes with the gases in the 5-l flask, circulates past the electrodes, condenses and empties back into the boiling flask. The U-tube prevents circulation in the opposite direction. The acids and amino acids formed in the discharge, not being volatile, accumulate in the water phase. The circulation of the gases is quite slow, but this seems to be an asset, because production was less in a different apparatus with an aspirator arrangement to promote circulation. The discharge, a small corona, was provided by an induction coil designed for detection of leaks in vacuum apparatus.

The experimental procedure was to seal off the opening in the boiling flask after adding 200 ml of water, evacuate the air, add 10 cm pressure of H_2, 20 cm of CH_4, and 20 cm of NH_3. The water in the flask was boiled, and the discharge was run continuously for a week.

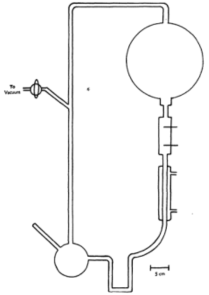

FIG. 1.

During the run the water in the flask became noticeably pink after the first day, and by the end of the week the solution was deep red and turbid. Most of the turbidity was due to colloidal silica from the glass. The red color is due to organic compounds adsorbed on the silica. Also present are yellow organic compounds, of which only a small fraction can be extracted with ether, and which form a continuous streak tapering off at the bottom on a one-dimensional chromatogram run in butanol-acetic acid. These substances are being investigated further.

At the end of the run the solution in the boiling flask was removed and 1 ml of saturated $HgCl_2$ was added to prevent the growth of living organisms. The ampholytes were separated from the rest of the constituents by adding $Ba(OH)_2$ and evaporating *in vacuo* to remove amines, adding H_2SO_4 and evaporating to remove the acids, neutralizing with $Ba(OH)_2$, filtering and concentrating *in vacuo*.

[1] National Science Foundation Fellow, 1952–53.

[2] Thanks are due Harold C. Urey for many helpful suggestions and guidance in the course of this investigation.

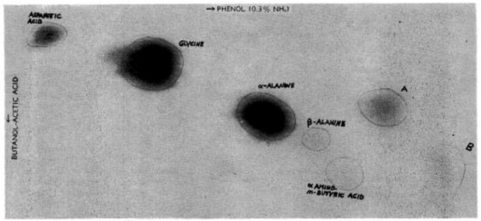

FIG. 2.

The amino acids are not due to living organisms because their growth would be prevented by the boiling water during the run, and by the $HgCl_2$, $Ba(OH)_2$, H_2SO_4 during the analysis.

In Fig. 2 is shown a paper chromatogram run in *n*-butanol-acetic acid-water mixture followed by water-saturated phenol, and spraying with ninhydrin. Identification of an amino acid was made when the R_f value (the ratio of the distance traveled by the amino acid to the distance traveled by the solvent front), the shape, and the color of the spot were the same on a known, unknown, and mixture of the known and unknown; and when consistent results were obtained with chromatograms using phenol and 77% ethanol.

On this basis glycine, α-alanine and β-alanine are identified. The identification of the aspartic acid and α-amino-*n*-butyric acid is less certain because the spots are quite weak. The spots marked A and B are unidentified as yet, but may be beta and gamma amino acids. These are the main amino acids present, and others are undoubtedly present but in smaller amounts. It is estimated that the total yield of amino acids was in the milligram range.

In this apparatus an attempt was made to duplicate a primitive atmosphere of the earth, and not to obtain the optimum conditions for the formation of amino acids. Although in this case the total yield was small for the energy expended, it is possible that, with more efficient apparatus (such as mixing of the free radicals in a flow system, use of higher hydrocarbons from natural gas or petroleum, carbon dioxide, etc., and optimum ratios of gases), this type of process would be a way of commercially producing amino acids.

A more complete analysis of the amino acids and other products of the discharge is now being performed and will be reported in detail shortly.

References

1. OPARIN, A. I. The Origin of Life. New York: Macmillan (1938).
2. UREY, H. C. *Proc. Natl. Acad. Sci. U. S.*, **38**, 351 (1952); *The Planets*. New Haven: Yale Univ. Press Chap. 4 (1952).
3. BERNAL, J. D. *Proc. Phys. Soc.* (*London*), **62A**, 537 (1949); **62B**, 597 (1949); *Physical Basis of Life*. London: Routledge and Kegan Paul (1951).

Manuscript received February 13, 1953.

A Vacuum Microsublimation Apparatus

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The analytical biochemist is frequently confronted with the task of isolating microquantities of substances in a chemically pure state from small quantities of tissues or biological fluids. Kofler (*1*) edited a book covering the use of microsublimation, melting point, eutectics, etc., in identifying microquantities of organic material. The advantages of sublimation over other methods of purification have been discussed by Hubacher (*2*). Many types of vacuum sublimation apparatus have been described (*1–3*). The equipment described here is inexpensive and can be assembled readily by any laboratory worker with a modicum of glassblowing skill.

To a thick-walled, round-bottom, Pyrex test tube, 30 × 200 mm, is attached a glass side arm about one in. from the bottom. Using a suspension of very fine emery in glycerin or fine valve-grinding compound, the open end of the test tube is ground against the aluminum block of a Fisher-Johns melting point apparatus (Fisher Scientific Co., St. Louis, Mo.) until it makes a vacuum-tight seal when dry. This is the vacuum hood. Microbeakers are prepared from flat-

[1] The author is indebted to Robert Puckett, of this laboratory, for technical assistance in preparing this apparatus.

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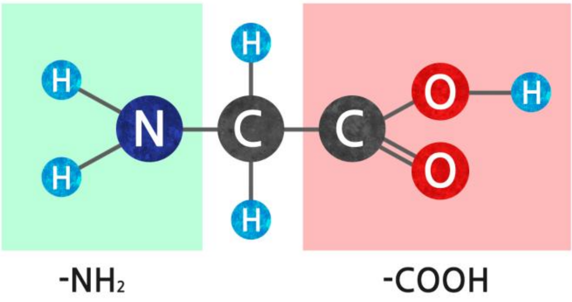
10-1 밀러의 반응물(Miller's Reactants)

생명의 기반으로 작용하는 유기화합물들이 지구의 대기가 이산화탄소, 질소, 산소, 물 대신 메탄, 암모니아, 물, 그리고 수소로 이루어졌을 때 만들어졌다는 생각은 오파린에 의해 제안되었고, 최근에 유리와 버날에 의해 강조되었다.

The idea that the organic compounds that serve as the basis of life were formed when the earth had an atmosphere of methane, ammonia, water, and hydrogen instead of carbon dioxide, nitrogen, oxygen, and water was suggested by Oparin and has been given emphasis recently by Urey and Bernal.



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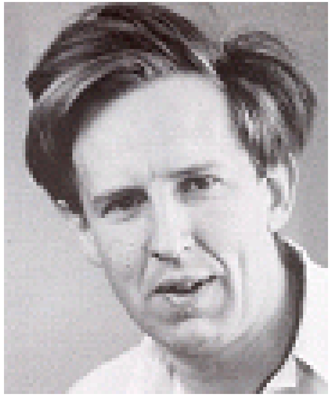
http://www.pensament.com/filoxarxa/imatges/Oparin.jpg

오파린
Alexander Oparin
1894-1980

<출처>
https://upload.wikimedia.org/wikipedia/commons/thumb/2/2e/Harold_Urey.jpg/200px-Harold_Urey.jpg

유리
Harold Urey
1893-1981



<출처>
http://79.170.40.183/grahamstevenson.me.uk/images/stories/bernaljd.jpg

버날
John Desmond Bernal
1901-1971

10-1 밀러의 반응물(Miller's Reactants)

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우주의 원자 존재 비

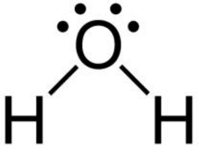
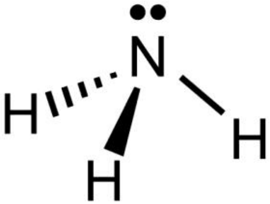
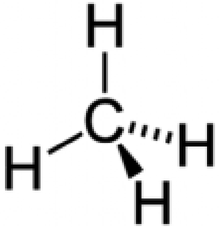
(수소 원자의 개수를 100만이라고 하면)

H	1,000,000	He	80,000
O	840	C	560
N	95		

우주의 분자 존재 비

(수소 원자의 개수를 100만이라고 하면)

H_2 CO N_2 H_2O	10 - 10,000
HCN CO_2 NH_3	~ 1
CH_4	< 1

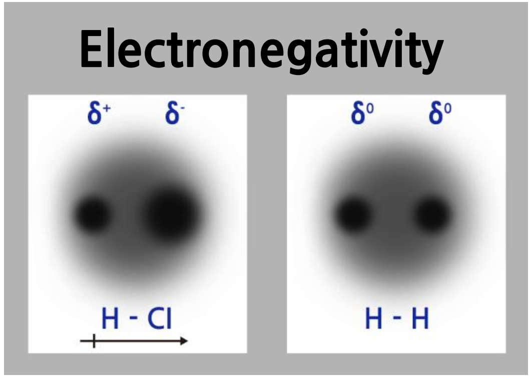





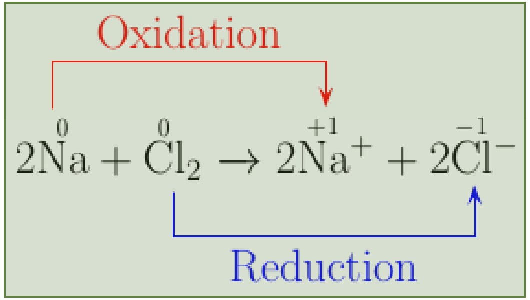
밀러가 사용한 네 가지 물질은 우주에 풍부하면서 단일결합 만으로 이루어진 분자들이다.

전기음성도 H < C << N < O

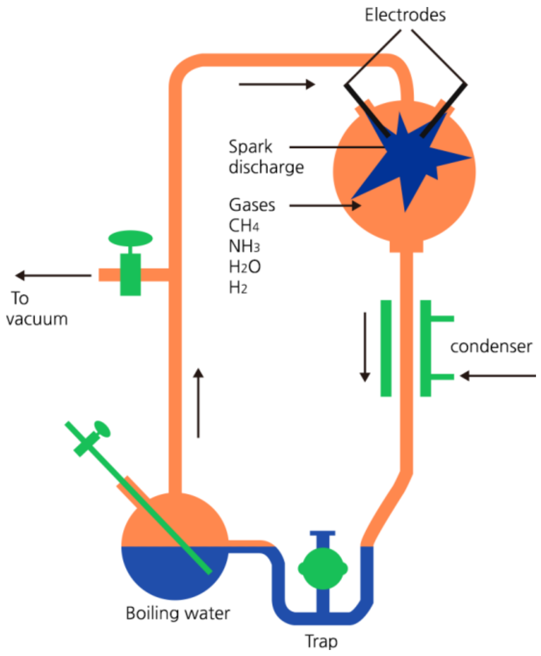
수소와 탄소는 전자를 내어주고,
질소와 산소는 전자를 끌어당긴다.

환원성	산화성	
CH_4	CO_2	탄소가 수소를 잃고 산소와 결합 : 산화
NH_3	N_2	질소가 수소를 잃음 : 산화
H_2O	O_2	산소가 수소를 잃음 : 산화
H_2	H_2O	수소가 산소와 결합 : 산화





이 가정을 테스트하기 위해 CH_4, NH_3, H_2O, 그리고 H_2를 전기 방전을 통해 순환시키는 장치를 만들었다.

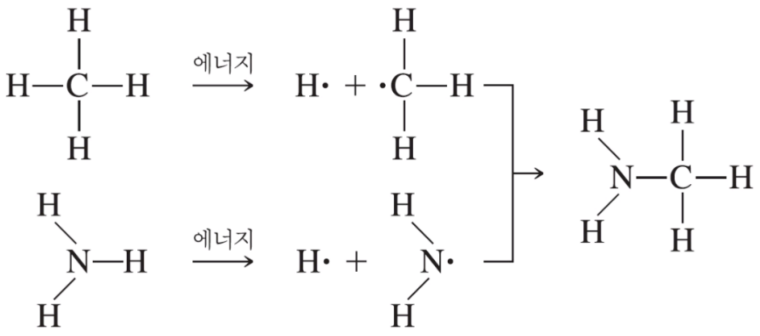


In order to test this hypothesis, an apparatus was built to circulate CH_4, NH_3, H_2O, and H_2 past an electric discharge.

플라스크에서 끓인 물은 5 리터 플라스크에서 다른 기체들과 섞여서 전극을 통해 순환하고, 응축되어 끓이는 플라스크로 되돌아간다.

Water is boiled in the flask, mixes with the gases in the 5-l flask, circulates past the electrodes, condenses and empties back into the boiling flask.

원시 대기에서 화합물들이 만들어지는데 전기 방전이 중요한 역할을 했을지도 모른다.



Electrical discharge may have played a significant role in the formation of compounds in the primitive atmosphere.

H-O bond energy : 467 kJ/mol

(467 kJ/mol)/6.022 x 10^{23}

= 7.75 x 10^{-19} J

E = hν   ν = E/h

ν = (7.75 x 10^{-19} J)/(6.626 x 10^{-34} J.s)

= 1.17 x 10^{15} s^{-1}

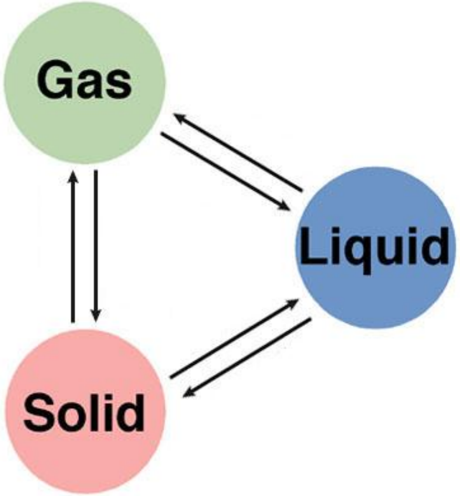
λ = (2.998 x 10^{8} m.s^{-1})/(1.17 x 10^{15} s^{-1})

= 2.56 x 10^{-7} m

= 256 nm (ultraviolet)

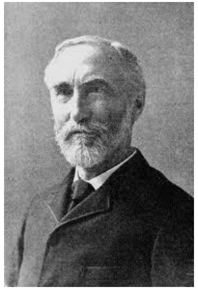
visible : 400 - 700 nm

열역학 : 반응의 방향성



Gibbs 자유에너지

모든 과정은 깁스 자유에너지가 감소하는 방향으로 자발적으로 진행한다.



<출처> https://upload.wikimedia.org/wikipedia/commons/c/c7/Josiah_Willard_Gibbs_-from_MMS-.jpg

$$\Delta G = \Delta H - T\Delta S$$

엔탈피(enthalpy) : H - 안정도의 척도
엔트로피 (entropy) : S - 무질서도, 자유의 척도

기체 상태의 물 분자들이 전기적으로 끌려서 액체 물이 되면 보다 안정되기 때문에 엔탈피가 감소하고 그 차이가 열로 나온다.
이 때 엔트로피는 감소하지만 낮은 온도에서는 엔탈피 효과가 엔트로피 효과보다 크기 때문에 수증기는 응축해서 물이 된다.
반대로 높은 온도에서는 엔트로피 효과가 더 중요해져서 물이 끓는다.
화학 반응에서도 엔탈피 효과와 엔트로피 효과가 합해져서 전체적으로 깁스 자유에너지가 감소하는 방향으로 반응이 진행한다.

하루 동안 순환을 계속하자 플라스크의 물이 눈에 띄게 핑크색이 되었고, 일주일 후에는 용액이 짙게 붉고 혼탁하게 되었다.
혼탁한 이유는 대부분 유리에서 나온 실리카의 콜로이드 때문이다.

During the run the water in the flask became noticeably pink after the first day, and by the end of the week the solution was deep red and turbid. Most of the turbidity was due to colloidal silica from the glass.

10-3 밀러의 생성물(Miller's Products)

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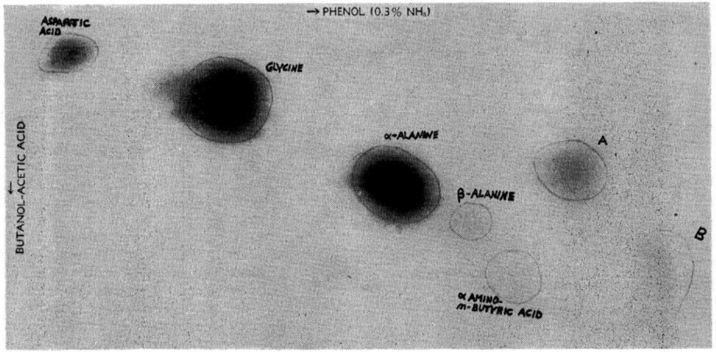
아래 그림은 n-부탄올-아세트산-물 혼합액, 그리고 다음에 물로 포화된 페놀로 전개하고 닌하이드린으로 스프레이해서 얻은 종이 크로마토그램을 보여준다.

In the figure below is shown a paper chromatogram run in n-butanol-acetic acid-water mixture followed by water-saturated phenol, and spraying with ninhydrin.



Stanley L. Miller, A Production of Amino Acids under Possible Primitive Earth Conditions, Science, New Series, Vol. 117, Issue 3046, May 15. 1953, p.528 - 529

10-3 밀러의 생성물(Miller's Products)

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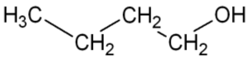
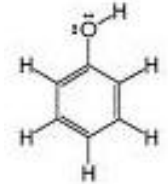
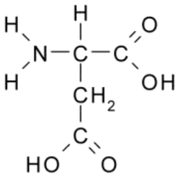
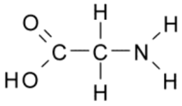
분배의 원리

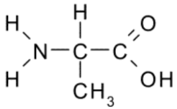
종이는 -OH기를 많이 가지고 있어서 극성이 높은 정지상이다. 1차원 분리에서 이동상으로 사용한 부탄올은 극성이 낮은 부틸기($-C_4H_9$)를 가지고 있다. 이동상이 모세관 현상에 의해 종이를 따라 이동할 때 극성이 낮은 메틸기($-CH_3$)를 가진 알라닌은 이동상에 보다 많이 분배되기 때문에 원점으로부터 보다 많이 이동한다.

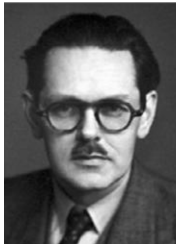

butanol


phenol


aspartic acid


glycine


alanine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https://upload.wikimedia.org/wikipedia/commons/thumb/d/df/Archer_John_Porter_Martin_Nobel.jpg/220px-Archer_John_Porter_Martin_Nobel.jpg

마틴 (Archer Martin, 1910-2002).
1952년 노벨 화학상을 수상했다.

Review

On top of the questionnaire
For Stanley Miller
And Harold Urey, his thesis advisor
Was how amino acids could appear
From the early atmosphere
And water
So that life could begin and prosper.
The idea of chemical evolution
Was launched by Oparin.
The key test was the production
Of the simplest amino acid glycine.