

# Significance of Solvated Electrons ( $e_{aq}^-$ ) as Promoters of Life on Earth

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**Abstract.** Based on the present state of knowledge a new hypothesis concerning the origin of life on Earth is presented, and emphasizes the particular significance of solvated electrons ( $e_{aq}^-$ ). Solvated electrons are produced in seawater, mainly by  $^{40}\text{K}$  radiation and in atmospheric moisture by VUV light, electrical discharges and cosmic ray. Solvated electrons are involved in primary chemical processes and in biological processes. The conversion of aqueous  $\text{CO}_2$  and  $\text{CO}$  into simple organic substances, the generation of ammonia from  $\text{N}_2$  and water, the formation of amines, amino acids and simple proteins under the action of  $e_{aq}^-$  has been experimentally proven. Furthermore, it is supposed that the generation of the primitive cell and equilibria of primitive enzymes are also realized due to the strong reducing property of  $e_{aq}^-$ . The presented hypothesis is mainly founded on recently obtained experimental results. The involvement of  $e_{aq}^-$  in such mechanisms, as well as their action as an initiator of life is also briefly discussed.

According to the current state of knowledge, the age of the earth is about 4.5 billion years. Up to 0.6 billion years, microorganisms were the only creatures populating the earth. This time period was followed by the epoch of the dinosaurs, various prehistoric animals and birds and later by mammals. At about that time, the first simple organic substances were formed in seawater and in the primitive atmosphere with moisture and were discharged by falling to the earth's surface.

There is considerable amount of literature concerning the origin of life on earth and numerous theories have been published, which will not be reviewed in the present article. However, a new concept regarding the generation of primitive organic compounds as the basis for the beginning

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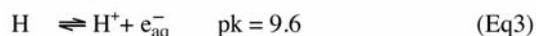
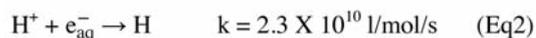
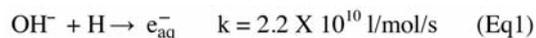
Key Words: Life on Earth, solvated electrons, primitive biological compounds.

of life, founded on the significant role and implication of 'solvated electrons' ( $e_{aq}^-$ ) is presented. It is also hypothesized that  $e_{aq}^-$  essentially acted as the 'spark' of life by the initiating primitive life on earth.

In the following, the generation and abundance of  $e_{aq}^-$  in seawater and in water contained as moisture in the primitive atmosphere is firstly discussed. After that, the formation of oxygen, nitric oxides *etc.* in the atmosphere, as well as the generation of simple organic compounds, such as aldehydes, carboxylic acids and simple proteins by possible chemical processes is mentioned. Finally, the genesis of the primitive living cell with the involvement of  $e_{aq}^-$  is hypothesized.

## Solvated Electrons ( $e_{aq}^-$ )

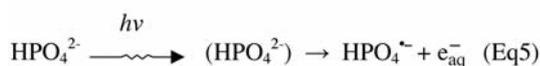
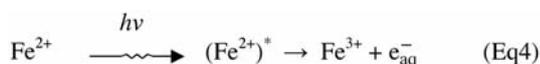
The existence of  $e_{aq}^-$  was first established by studying the conversion of aqueous carbon dioxide into simple organic compounds under irradiation with  $\gamma$ -rays (1), as well as with UV light (1, 2). The absorption spectrum of  $e_{aq}^-$  in aqueous solution at room temperature with a maximum at 720 nm was determined by pulse radiolysis (3). The absorption of trapped electron ( $e_{tp}^-$ ) in ice-matrix (77°K) of alkaline aqueous solution was found to occur at 530 nm (4). The  $e_{aq}^-$  thus represents a thermalized electron ( $e_{tt}^-$ ;  $E \leq 10$  eV;  $1$  eV = 23 kcal/mole) embedded in a shell of positive dipoles of water molecules (or other polar liquids) within about  $0.3 \times 10^{-12}$  s. The  $e_{aq}^-$  is a strongly-reducing entity, representing the basic form of an H-atom, whereas the last one is the acidic form of the reduction species (5).



## Generation of $e_{aq}^-$ in Seawater

Natural radioisotopes contained in seawater, *e.g.*  $^{40}\text{K}$ , and cosmic rays can generate  $e_{aq}^-$  in seawater. As reported

previously,  $^{40}\text{K}$  acts as principal radiation source of  $e_{\text{aq}}^-$  in seawater, having a half-life of  $1.3 \times 10^9$  years, where 30% has a maximum  $\beta$ -ray energy of 1.32 MeV (6). Taking the G value as 2.6 (where G is number of species formed or decomposed per 100 eV energy absorbed) at a mass of the oceans of  $1.4 \times 10^{24}$  g and a production rate of  $1.3 \times 10^2$   $e_{\text{aq}}^-/\text{g/s}$ , the global production from  $^{40}\text{K}$  is  $1.3 \times 10^2$  moles of  $e_{\text{aq}}^-/\text{s}$  (6). The same author also considered  $e_{\text{aq}}^-$  production by cosmic rays absorbed by seawater at a rate of  $1.5 \times 10^3$   $e_{\text{aq}}^-/\text{g/s}$ , hence cosmic rays contribute about 4% to that of  $^{40}\text{K}$ . The total permanent amount of  $e_{\text{aq}}^-$  in the oceans is estimated on the basis of pulse radiolysis experiments to be  $8 \pm 2 \times 10^{-5}$  mol (6). Additional  $e_{\text{aq}}^-$  production is achieved by solar energy ( $\lambda > 300$  nm) absorbed by inorganic ions in seawater, such as  $\text{Fe}^{2+}$  and  $\text{HPO}_4^{2-}$ .



It was also found that natural minerals acting as semi-conductors, e.g.  $\text{TiO}_2$  (rutil) as aqueous suspension can photolyse water, forming  $e_{\text{aq}}^-$ , OH and H species (7-10).  $\text{TiO}_2$  has a bandgap ( $E_G \approx 3.1$  eV), which corresponds to the absorption of sunlight of  $\lambda \approx 400$  nm. The photoaction of  $\text{TiO}_2$  is schematically illustrated in Figure 1. Thereby, the electrons of the illuminated part of a  $\text{TiO}_2$  particle move to the shaded side and are ejected in water as  $e_{\text{aq}}^-$ . The remaining positively charged ‘holes’ on the illuminated  $\text{TiO}_2$  surface react with water forming OH radicals. Hence, each  $\text{TiO}_2$  particle produces reducing ( $e_{\text{aq}}^-/\text{H}$ ) and oxidizing (OH) species under the influence of sunlight as well as ionizing radiation. It is conceivable that on the catalytic surface of semi-conductors in seawater primary chemical processes can be initiated, e.g. formation of simple organic compounds by  $\text{CO}_2$  reduction (9, 10).

### Generation of $e_{\text{aq}}^-$ in the Atmosphere

Atmospheric water can be degraded under the influence of the vacuum-UV part of the solar energy (VUV light,  $\lambda < 200$  nm) Table I. In addition, electrical discharges and cosmic rays contribute to the generation of  $e_{\text{aq}}^-$  in the atmosphere. These processes can in general be expressed by the following reactions:

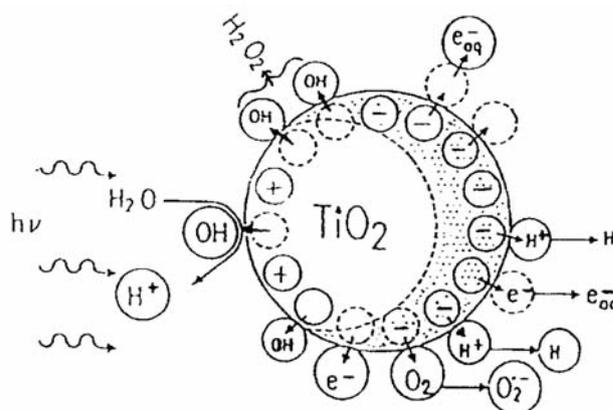
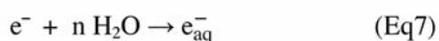


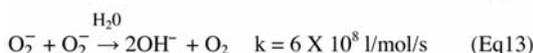
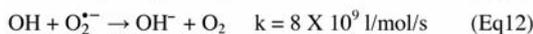
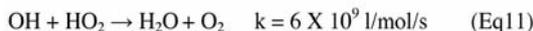
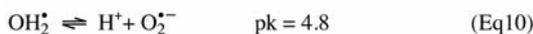
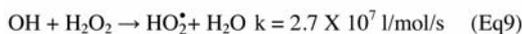
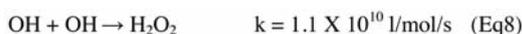
Figure 1. Formation of free radicals on surface of  $\text{TiO}_2$  under the influence of sunlight as well as by ionizing radiation (7, 9).

It has been experimentally shown that liquid water is photolyzed by VUV light into  $e_{\text{aq}}^-$ , H and OH species (11). The quantum yields of the primary products resulting from VUV photolysis are shown in Table I.

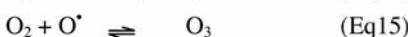
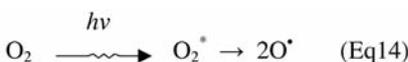
The yield of water degradation products resulting from electrical discharges and cosmic rays in the atmosphere remains unknown.

### Formation of Oxygen

It is conceivable that the primitive atmosphere contained different gases, amongst which oxygen was found. Oxygen might also be formed as a product of water photolysis according to the following reactions (Eq8 to 13) (5):



Similar reactions can also proceed by water degradation at higher temperatures during formation of the earth incrust and from volcanic lava. Simultaneously with these processes, ozone ( $\text{O}_3$ ) might also be generated.

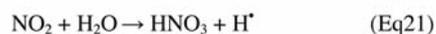
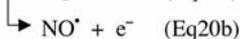
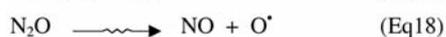
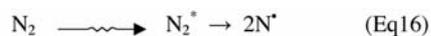


Very probably, photochemical reactions initiated by VUV light, electrical discharges and cosmic rays have also

contributed to the  $O_2$  formation by splitting of water contained in the atmosphere.

### Nitrogen Oxides and Acids

Nitrogen has a triple bond between the nitrogen atoms and is a very stable molecule ( $D_1=9.756$  eV). However, by the action of VUV light, cosmic rays and electrical discharges in the atmosphere, the  $N_2$  molecule can be split. The resulting  $N^*$  atoms can react with  $O_2$  forming a variety of oxides, which by reaction with water result in the corresponding acids:

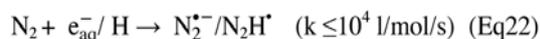


According to similar reactions sulfuric, phosphoric and other acids can be also formed in the atmosphere. Such processes could proceed in seawater, initiated by cosmic rays and by radiation from natural radioisotopes.

It should be mentioned that during the incrustation period of the earth nitrogen was very likely bound as nitrides, which now days are still contained in granite. At the edge of volcanic lava, ammonium chloride is formed, which may have contributed to the initial formation of amino acids.

### Ammonia

The formation of ammonia from high purity nitrogen and triply distilled water (pH  $\sim 7.5$ ) under the influence of VUV light and  $\gamma$ -ray has been reported (13). As measured using pulse radiolysis, the rate constant of the reaction  $e_{aq}^-/H$  with nitrogen is extremely low:



These findings, however, emphasize the possible generation of amines, amino acids and simple proteins under primitive conditions. It is also conceivable that other kinds of energy, such as high temperatures, might have contributed in this respect (see also equation 16).

### Organic Compounds

It is supposed that the primordial seawater and atmosphere contained  $CO_2$ ,  $CO$ ,  $SO_2/SO_3$  etc., which by reactions with

Table I. Primary products of water photolysis at 123.6, 147 and 184.9 nm vacuum UV (VUV) light (11).

VUV light (nm/eV)	Q values		
	$e_{aq}^-$	H	OH
133.6/10.0	0.120	1.0	1.0
147/8.4	0.075	0.72	0.72
185/6.7	0.040	0.33	0.33

1eV=23kcal/mol. Q value=number of species formed by absorption of 1 quant (hr) of VUV light.

the primary products of water radiolysis and photolysis ( $e_{aq}^-$ , H, OH) are converted into simple organic compounds. As already mentioned,  $CO_2$  acts as a very efficient scavenger of  $e_{aq}^-$ , which led to the discovery of the existence of  $e_{aq}^-$  (1). The reaction mechanisms of  $CO_2$  and  $CO$  conversion into organic compounds has been studied in detail (1, 2, 9, 10, 14-16). Some basic reactions in this respect are presented in Table II.

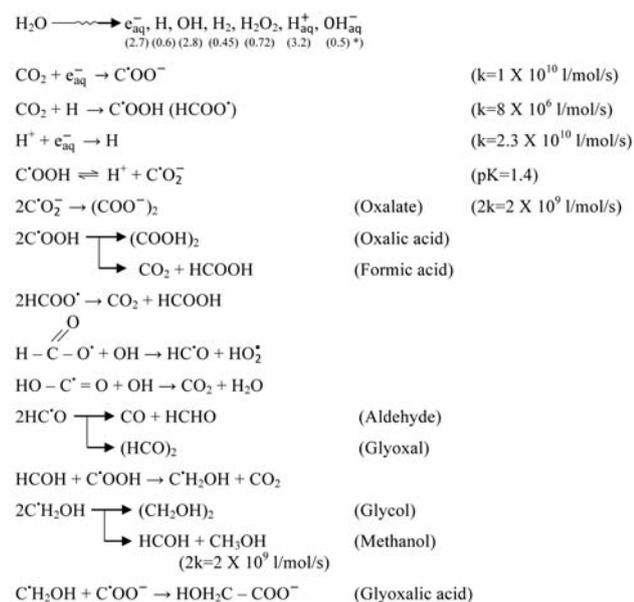
These processes can also proceed in the atmosphere, as well as in seawater, by initiation of the above mentioned energy sources.

$CO_2$  and  $CO$  reduction can also occur on the surface of semi-conductor particles, e.g.  $TiO_2$  (7, 9) as shown by the reactions given in Table III.

### Amines, Amino acids, Simple proteins

Based on the above presented results,  $CO_2$  and  $CO$  can be reduced under primitive conditions by  $e_{aq}^-$  to simple organic compounds, including, but not limited to, aldehydes, carboxylic acids and alcohols. In addition ammonia can be converted to amines and other ammonium compounds. All these substances derived from  $CO_2$ ,  $CO$  and ammonia can lead to the corresponding free radicals and finally to the formation of amines and amino acids. It has been shown experimentally that amines in the presence of  $CO_2$  or carbonate can be carboxylated to amino acids. Furthermore, carboxylic acids in ammonia-containing aqueous media likewise are converted to amino acids (17-21). It has also been found that several amino acids are formed by carboxylation of specific amines. This fact demonstrated that the attack of free radicals may occur at different positions of the amino molecule, resulting in a variety of free radicals and consequently in the corresponding amino acids. For example, the carboxylation of ethylamine results in the generation of seven amino acids depending on the respective radiation dose absorbed, of which  $\alpha$ -aminobutyric acid gives the highest yield. In addition to this, norvaline and proline production were also determined (20). Experiments showed that the

Table II. Water radiolysis and radiation-induced conversion of CO<sub>2</sub> into simple organic compounds.



\*G-values-number of primitive products formed by 100eV absorbed energy are given in brackets.

formation of proline starts with alkylation of alanine to norvaline, followed by cyclization of the norvaline radical to give proline, as shown in Figure 2.

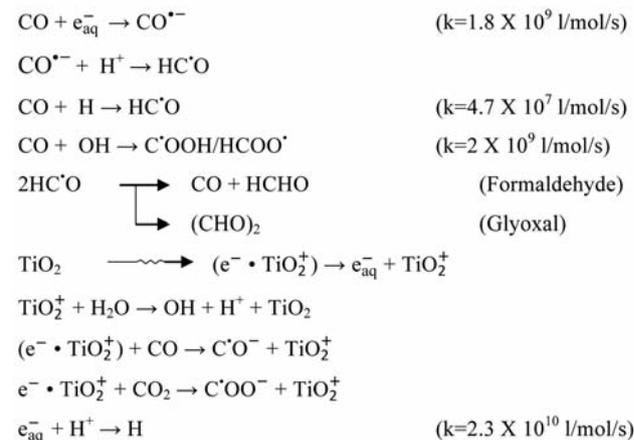
Amino acids can also be formed by carboxylation of amines under the action of VUV light (21). Further experimental results demonstrated that radiation-induced carboxylation of ethylamine in aqueous solutions containing sodium sulfide or hydrogen sulfide leads to the formation of cystine, cysteine and cysteic acids in addition to  $\alpha$ - and  $\beta$ -alanine and glycine (22).

It should be mentioned that the free radicals formed by prolonged radiation of primary-obtained amino acids lead to the formation of simple proteins (23). Further reactions of protein free radicals can result in the formation of large protein molecules, which tend to form associates (unstable complexes) and hence may act as precursors of cell components.

### The Spark of Life

As established by experiments, organic substances with functional groups such as  $-\text{OH}$ ,  $-\text{O}^-$ ,  $-\text{COO}^-$ ,  $-\text{NH}_2$ ,  $-\text{NHCH}_3$ , can eject  $\text{e}_{\text{aq}}^-$  in aqueous solution when excited into the singlet state (24). The same effect was also observed for hormones (25-27), vitamins (28) *etc.* It should be mentioned that substances ejecting  $\text{e}_{\text{aq}}^-$  can also consume part of these (rate constant,  $k \geq 10^9$ - $10^{10}$  l/mol/s) as well as transfer these electrons

Table III. Some basic reactions of CO reactions in aqueous media as well as on TiO<sub>2</sub>-surface.

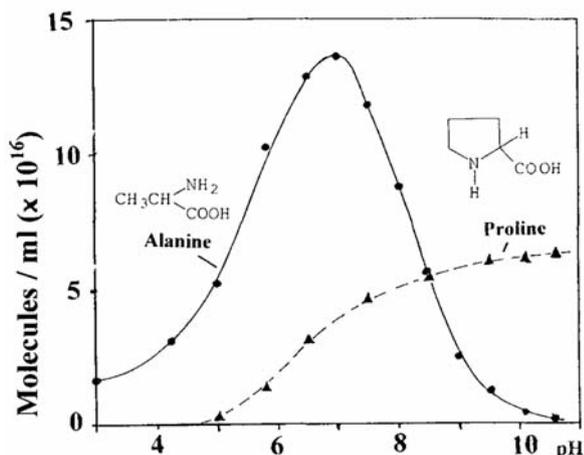
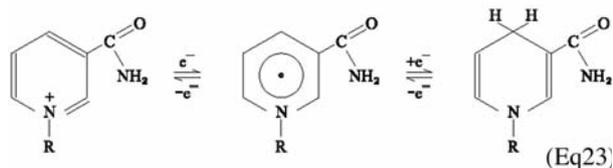


to other substances, and thus act as electron mediators (25, 27). Thereby the emitted  $\text{e}_{\text{aq}}^-$  preserve the specific frequency of the 'mother molecule' during the transfer process to, for example, the receiving centres in the brain (26). Based on the specific frequency of  $\text{e}_{\text{aq}}^-$  the brain is able to determine the origin of the message and can act correspondingly. This process enables communication between biological systems.

Supposing that primitive organic substances become electronically-excited upon energy absorption and hence, likewise, are able to eject, consume and transfer  $\text{e}_{\text{aq}}^-$  to other primitive compounds, this would represent the first step in the generation of life.

On the other hand it is known that organic substances with large molecules, including hormones (27), tend to form associates (unstable complexes) at concentrations of  $\geq 10^{-7}$  mol/l. Hence, it can be hypothesized that this tendency is also true for primitive organic compounds, leading to the formation of pseudo-bioassociates, which are involved in functioning equilibria.

As mentioned above, the synthesis of organic compounds, which are assumed to be the basis for generating the scaffold of a primitive cell, can be explained by laboratory experiments. However, the 'spark of life' for the appearance of living cells still remains Nature's secret. Very probably the cell scaffold could have been created by chance, originating from associated amino acids that formed proteins and simple enzymes as well as redox systems in which  $\text{e}_{\text{aq}}^-$  played a decisive role. It is then hypothesized that under these primitive conditions, a biosystem similar to nicotinic amide-adenine-dinucleotide-hydride (NADH; coenzyme 1) can be formed. NADH is considered the most important co-enzyme, and drives the reduction and oxidation processes in the cell and is the most efficient antioxidant. The equilibria involving  $\text{e}_{\text{aq}}^-$  are shown by the following (Eq23):



**Radiation - induced formation of alanine and proline from 0.1 mol/dm ethylamine and  $0.25 \times 10^{-3}$  mol/dm  $\text{CO}_2$  as a function of the PH-value of the aqueous solution. Absorbed dose:  $7.2 \times 10^{19}$  eV/ml**

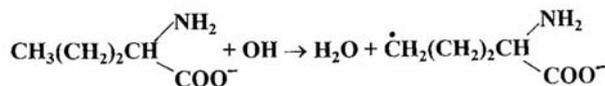
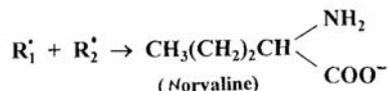
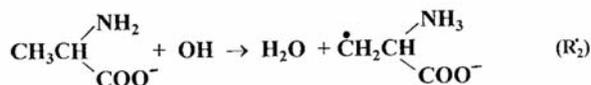
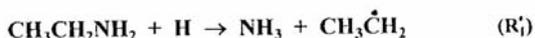


Figure 2. Formation of proline by cyclization of norvaline radical, resulting from ethylamine and alanine.

NAD, nicotinamide-adenine- dinucleotide and R, adenosine-diphosphor-ribose. In other words, based on their unique properties,  $e_{aq}^-$  can be considered as the species initiating and driving factors for the start of life in primitive cells.

## Conclusion

The presented data concerning the origin of life on Earth are founded on the unique properties of  $e_{aq}^-$ . They are produced in seawater mainly by the action of  $^{40}\text{K}$  radiation, cosmic rays and natural semi-conductors such as  $\text{TiO}_2$  under the influence of sunlight. In atmospheric moisture,  $e_{aq}^-$  are generated under the influence of VUV light, electrical discharges and cosmic rays. Moreover it is shown that  $e_{aq}^-$  can convert  $\text{CO}_2$  and  $\text{CO}$  into simple organic compounds. They are involved in the formation of ammonia from  $\text{N}_2$  and water and in the production of amines, amino acids and simple proteins. The formation of oxygen, nitrous oxides in seawater and in the atmosphere is also mentioned. Finally, the action of  $e_{aq}^-$  as the 'spark of life' by initiating equilibria of simple enzymes in primitive cell systems, similar to that of NAD and its hydride form NADH is hypothesized.

This new hypothesis is based on laboratory experiments. However, questions remain with respect to the origin of life that should be pursued in further studies.

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