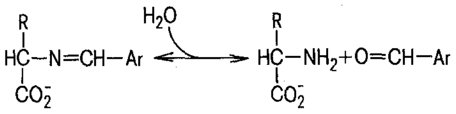
This tautomery of the Schiff base is finally completed here by hydrolysis of the new imino group, as:



$$HC(R)(CO_2^-)-N=CH-Ar \xrightarrow{H_2O} HC(R)(CO_2^-)-NH_2+O=CH-Ar$$

In some cases, the same process is applied from simpler reagents without any final separation into 2 products.

Particularly typical in this respect is the case of far-from-equilibrium hydroxylation of initially non oxidized C atoms, which can even occur non enzymatically in sensible positions of aromatic structures. Such reactions appear to be driven by any process having produced HO˙ radicals in a previous step, e.g., from reduction of dissolved O_2 to H_2O_2 followed by any catalytic dissociation of the peroxide bond[7]. Such radicals can then attack the RH bond, as:

$$RH + {}^{\cdot}OH \rightarrow R^{\cdot} + H_2O$$

followed by:

$$R^{\cdot} + {}^{\cdot}OH \rightarrow ROH$$

or

$$R^{\cdot} + HOOH \rightarrow ROH + {}^{\cdot}OH$$

finally resulting in the global oxidation:

$$\begin{cases} RH + H_2O \rightarrow ROH + 2\,e^- + 2\,H^+ \\ H_2O_2 + 2\,e^- + 2\,H^+ \rightarrow 2\,H_2O \end{cases}$$

i.e.

$$RH + H_2O_2 \rightarrow ROH + H_2O$$

which globally performs a redox reaction involving modifications of covalent topologies of both implied reagents, without involving at any time any intermolecular electron transfer, forbidden because it proceeds too fast to be simultaneous with a change in the covalent vicinity between relatively heavy and too inert atoms.

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Electrochemical energetics of the biosphere

by René Buvet

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1. *Energy balances involved in the building or the degradation of biochemical compounds*

Numerical data related to standard free enthalpies of formation of organic compounds from elements are available for a set of simple carbonaceous chemicals in their pure states[1]. These chemicals can be considered as roughly representative of more complex biochemicals owing to the additivity of energy balances involved in the building up of linkages which are not closely adjacent in molecules. Considering the compared order of magnitudes of energy balances involved in the formation of covalent bonds in these compounds and of their possible solution and interaction energies in aqueous phases, these numerical data, though related to the pure states of compounds, also represent a reasonable approximation of those involved in the formation of these compounds in aqueous phases in biological systems. It is well known that many of these standard free enthalpies of formation of carbonaceous chemicals from graphite and gaseous oxygen, hydrogen and nitrogen in their standard states are negative, which simply means that these compounds are energetically more stable than the elements, and that only some are positive, concerning mainly unsaturated organics, which means that even their formation from elements should involve some kind of external energy supply.

However, it must be emphasized that 3 groups of global organic syntheses always present positive free enthalpy balances near ambient temperature and pressure.

This is the case for any synthesis from the most hydrogenated forms of carbon, oxygen and nitrogen, i.e., $CH_4\nearrow$, H_2O and $NH_3\nearrow$. All the reactions such as:

$$x\,CH_4\nearrow + z\,H_2O + t\,NH_3\nearrow \longrightarrow C_xH_yO_zN_t + \frac{4x+2z+3t-y}{2}H_2\nearrow,\ \Delta G^\circ_{S.H.}$$

have positive standard free enthalpy balances. Hence, in the presence of any excess of hydrogen, such as could have occurred on the primitive earth or occurs in the external atmosphere of giant planets, the complete equilibrium state of any carbonaceous system, not too far from ambient temperature and pressure, contains mainly methane, water and ammonia, with only very small amounts of some other compounds, e.g., ethane and nitrogen, having the lowest standard free enthalpies of syntheses from such a hydrogenated system ($\Delta G^\circ_{S.H.}$). All other carbonaceous chemicals, including biochemicals, need more or less energy for being produced. As a mean value, the incorporation of one supplementary heavy atom such as C, O or N, with only a single bond needs between 8 and 20 kcal · at · g^{-1} (Buvet[2]).

But all reactions such as:

$$x\,CO_2\nearrow + \frac{y}{2}H_2O + \frac{t}{2}N_2\nearrow \longrightarrow C_xH_yO_zN_t + \frac{2x+y/2-z}{2}O_2\nearrow,\ \Delta G^\circ_{S.O}$$

also exhibit positive values of standard free enthalpy, as is better known since they are in fact the inverse of combustions of organic chemicals. Then, in the presence of any sufficient amount of oxygen near ambient temperature and pressure, $CO_2\nearrow$, H_2O and $N_2\nearrow$ are the major components in the equilibrium state. In fact this predominance is here even stronger than previously, owing to the higher values of $\Delta G^\circ_{S.O.}$. The synthesis of any biochemical from these available lowest energy sources of inorganic carbon, hydrogen, oxygen and nitrogen on the earth today needs energy globally, which is supplied from some sort of biochemical accumulation of available physical energy, currently termed photosynthesis when performed from solar energy. Reciprocally, any complete aerobic destruction of biochemicals produces energy until carbon dioxide, water and nitrogen are produced.

Finally, it must be also remarked that all complete redox dismutations of carbonaceous compounds, which can always be written as:

$$8x\,C_xH_yO_zN_t + 2x(4x-y-2z+3t)H_2O \longrightarrow x(4x+y-2z-3t)CH_4\nearrow + x(4x-y+2z+3t)CO_2\nearrow + 8xt\,NH_3,\ \Delta G^\circ_D,$$

with the exception of the case of graphite itself, also imply positive values of standard free enthalpies of dismutation, ΔG°_D. It means here that, after having been synthesized from either the primitive or the contemporary earth, all biochemicals, if isolated from the surrounding excess of hydrogen or oxygen, should achieve complete dismutation to the states of methane, carbon dioxide and nitrogen. Such is, more or less quantitatively the case when methanogenic anaerobic fermentations of biological mixtures of compounds are performed.

All mentioned general results, obtained from a very simple exploitation of available energy data, are in fact summarized and biologically oriented forms of more complex calculations, performed with computers, which have established that in systems made from any given atomic fractions of C, H and O, only CH_4, CO_2, H_2O and the elements themselves can exist as major components at the complete equilibrium of the systems concerned near ambient temperature and pressure[3].

2. *Redox global levels and energetic stability of biochemicals*

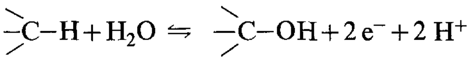
If one considers that, for the kind of functional groups which are involved in biochemicals, the total number of electron pairs that must be evolved from methane for producing a given compound, which can be defined as the total oxidation degree of the compound from methane, is obtained by adding:

- the number of bonds of carbon atoms in this compound to heteroatoms (O, S, N)
- plus the number of σ or π C–C-bonds,

it simply appears that:

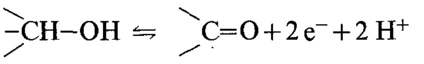
- the process of emergence of life from the equilibrium state in any hydrogenated environment where carbon would be available as methane, is globally an oxidation of carbon;
- the process of production of living organisms from the highest oxidation degree of carbon implied in CO_2, i.e., 4, is globally, as it concerns carbon, a reduction;
- any anaerobic fermentation is a redox dismutation of involved carbonaceous compounds, some increasing their oxidation degree and some decreasing it.

The comparison of these redox balances with previously recalled energetic ones leads to the general conclusion that the average degrees of oxidation of carbon atoms present in biochemicals, intermediate between 0 and 4 corresponding respectively to methane and carbon dioxide, are energetically unstable. This conclusion generalizes the well known similar one that is valid only for the more restricted case of transformations without any change of the carbon backbone and is related to the interversion of normal apparent potentials of successive bielectronic transitions of carbon atoms. In fact, it appears from available data that all transitions from any locally reduced carbon atom to one belonging an alcohol as:



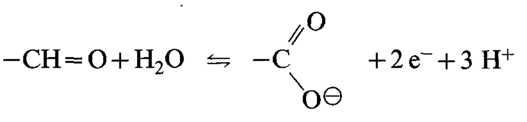
$$\geq C{-}H + H_2O \rightleftharpoons \geq C{-}OH + 2e^- + 2H^+$$

should occur at the equilibrium between +0.05 and +0.25 V/S.H.E at pH 7, although the corresponding equilibrium potentials range between −0.05 and −0.25 V/S.H.E. for redox transitions from alcohols to aldehydes or ketones as:



$$\geq CH{-}OH \rightleftharpoons \geq C{=}O + 2e^- + 2H^+$$

and are circa −0.5 or −0.6 V/S.H.E. as it concerns the transitions from aldehydes to carboxylates as:



$$-CH{=}O + H_2O \rightleftharpoons -C{\overset{\displaystyle /\!/ O}{\underset{\displaystyle \backslash O^{\ominus}}{}}} + 2e^- + 3H^+$$

and around the same value (−0.5 V/S.H.E) for the particular case of the transition from formate to bicarbonate.

In conclusion, all intermediate redox states in carbonaceous compounds, e.g., all stoichiometrically possible ones except the most oxidized and reduced ones are energetically unstable when C−C bonds are kept unchanged in the compounds considered, and should disappear by redox dismutation leading only to alkanic and carboxylic or carbonic carbons. This point is only currently partly taken into consideration as it concerns the well known Cannizzaro dismutation of aldehydes. As previously shown here, this should even be ultimately followed by backbone degradation leading to methane and carbon dioxide.

3. *Electrochemical principles involved in primitive and contemporary photosyntheses*

Assuming that the synthesis of biochemicals occurred at the periphery of the primitive earth under the influence of solar energy and from a state of more or less equilibrium in the presence of some excess hydrogen remaining from a protoplanetary cloud, it has been shown from laboratory experiments simulating the short term chemical evolution of such systems[2] that, if not considering the possible occurrence of inorganic photosensitizers, the only way to absorb any kind of energy from the pristine atmospheric phase of such a system leads to the excitation and even the ionisation to CH_4^+ with UV-radiation between 150 and 100 nm[4]. From such completely or nearly ionized states of CH_4, reaction pathways involving radical reactions into gas phases lead to complex mixtures of compounds containing mainly 2 or more atoms of C and N, such as C_2, C_3 and even C_4 saturated or unsaturated hydrocarbons, nitriles such as cyanhydric acid and other simple ones, e.g., acetonitrile, together with thiols and CS_2 when SH_2 is initially present[5,6]. These compounds represent an important increase of the oxidation level of carbon in the system, here merely offset by a strong production of hydrogen, as globally:

$$CH_4\nearrow + NH_3\nearrow \longrightarrow \text{Atmospheric precursors} + H_2\nearrow, \; \Delta G^\circ_{S.H.}$$

with strongly positive standard free enthalpy balances. A part of these atmospheric precursors is soluble in aqueous solutions where nucleophilic additions of, e.g., H_2O, NH_3, HCN, phosphates, thiols, etc. ... can occur at polarized multiple bonds of nitrile, aldehyde and produced imine groups. This leads to the relaxation of a part of the energy stored and to some increase of the molecular weight in produced carbonaceous compounds, which finally produce biochemicals further degradation of which is very low. Some condensed energy-rich derivatives of biochemicals, such as organic phosphates and peptide compounds are even produced by addition of thiols or phosphates or other present nucleophilic reagents on nitrile and imino groups[2,7,8].

At the very beginning of the chemical evolution of a planetary periphery starting from the hypothetically simplest atmosphere containing only H_2, CH_4 and small amounts of H_2O and NH_3, some UV-radiation of wavelength 150–190 nm could have penetrated into the underlying condensed aqueous phases where it could have been absorbed with the possible production of O_2 and H_2. However, the formation of atmospheric precursors should have implied the absorption of these wavelengths within the atmosphere.

The role of UV-radiation of wavelength larger than 200 nm should be also considered. In this respect, it is known[9] that the UV-spectrum of any simple monoelectronic reducer, such as transition cations M^{n+} which gives:

$$M^{n+} \rightleftharpoons M^{(n+1)+} + e^-, \; U^\circ$$

presents in aqueous solution a terminal absorption corresponding to the production of hydrated electron e^-_{aq} as:

$$M^+ \longrightarrow M^{(n+1)+} + e^-_{aq} \,.$$

This process corresponds to a positive free enthalpy:

$$\Delta G^\circ_e = F(U^\circ - (-2.7))$$

where - 2.7 V/S.H.E is the normal potential of e^-_{aq}.

This implies the absorption of UV-wavelength such as:

$$Nh\nu \geqslant \Delta G^\circ_e$$

and could be followed by:

$$e^-_{aq} + H^+ \longrightarrow H^\bullet \longrightarrow \frac{1}{2} H_2\nearrow$$

and

$$2\,M^{(n+1)+} + H_2O \longrightarrow \frac{1}{2} O_2\nearrow + 2\,H^+ + 2\,M^{n+}\,.$$

However, such an endergonic dismutation of H_2O, which is experimentally known with solutions of free or complexed transition metal redox couples supplied with far UV-light[10] is, in fact, energetically possible in the neutral range of pH, notwithstanding even more restrictive kinetic considerations, only if, at least:

$$U^\circ \gg U^{\circ\prime}_7 (O_2\nearrow/H_2O) = +0.81\ \text{V/S.H.E.}$$

which implies:

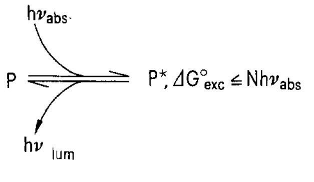
$$Nh\nu \geqslant \varDelta G^\circ \gg (0.8+2.7)\,F$$

or numerically:

$$\lambda \ll 340\ \text{nm}.$$

This shows that, because of the large overpotential which is implied in the oxidation of H_2O, such processes could not account for the contemporary photosynthesis which occurs from radiations with much larger wavelengths.

Finally, such so-called visible wavelengths can only be absorbed in aqueous solutions by organic or metallo-organic polyconjugated photoreceptors, P, leading more or less directly to the formation of electronically excited singlet or triplet first excitation states as:



which can be defined by the macroscopic standard free enthalpy balance $\varDelta G^\circ_{exc}$.

If, as is the case for P_{700} and P_{680} pigments involved in the photosystems I and II of higher plants, P is a monoelectronic reducer from its fundamental state:

$$P \rightleftharpoons P^+ + e^-, U^\circ(P^+/P)$$

as far as P^+ is also the oxidant involved in its oxidation from the excited state:

$$P^* \rightleftharpoons P^+ + e^-, U^\circ(P^+/P^*)$$

it is easily shown that:

$$U^\circ(P^+/P) - U^\circ(P^+/P^*) = \frac{\varDelta G^\circ_{exc}}{F} = \frac{\varDelta G^\circ_{exc}(\text{kcal} \times \text{mole}^{-1})}{23.05}.$$

Differences of more than 1 V between $U^\circ(P^+/P)$ and $U^\circ(P^+/P^*)$ can here be theoretically easily obtained, since $Nh\nu$ reaches about 50-60 kcal · mole^{-1} for wavelengths in the medium visible range. Experimental evidence has shown that this is effectively the case for biological photoreceptors P_{700} and P_{680} as well as for many organic reducing dyes such as semiquinones or redox mediators currently used in biochemical technology.

Now, if the radiative life-time of P* is large enough for keeping it at a chemically noticeable concentration under currently available solar light flux (mean value against time is about 200 $W \times m^{-2}$ in temperate regions), which is accessible with some excited states and preferably triplet ones, a chemical de-excitation:

$$P^* + Ox_1 \longrightarrow P^+ + Red_1$$

can occur in the presence of any monoelectronic oxidant Ox_1, such as:

$$U^\circ(Ox_1/Red_1) \geqslant U^\circ(P^+/P^*)\,.$$

An immediate convenient evacuation of Red_1 is then necessary for avoiding any backreaction with P^+.

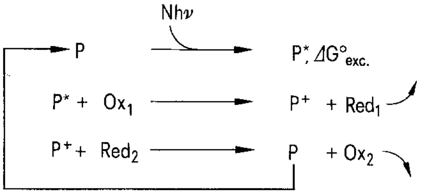
This oxidant is then able to oxidize any monoelectronic reducer Red_2 as:

$$P^+ + Red_2 \longrightarrow P + Ox_2$$

if

$$U^\circ(P^+/P) \geqslant U^\circ(Ox_2/Red_2)\,.$$

Finally, the cycle:



which is globally equivalent to the redox reaction:

$$Ox_1 + Red_2 \longrightarrow Red_1\nearrow + Ox_2\searrow\ ,\ \varDelta G^\circ_r$$

leads to a photochemical accumulation of energy[11]

$$\varDelta G^\circ_r = F\,(U^\circ(Ox_2/Red_2) - U^\circ(Ox_1/Red_1))$$

if

$$U^\circ(P^+/P) > U^\circ(Ox_2/Red_2) > U^\circ(Ox_1/Red_1) > U^\circ(P^+/P^*)$$

with all wavelengths such as:

$$Nh\nu \geqslant \varDelta G^\circ_{exc} = F\,(U^\circ(P^+/P) - U^\circ(P^+/P^*)).$$

This could easily be the case, since U° differences of more than 1 V are currently observed in photoelectrochemical experiments. It is known that in higher plants, 2 such cycles occur, respectively named photosystems I and II, associated through an electron transfer chain, by:

$$P_{700} + P^{*}_{680} \longrightarrow P_{700} + P^{+}_{680}$$

in such a way that it leads to the global endergonic redox reaction:

$$NAD(P)^{+} + H_2O \longrightarrow NAD(P)H + \frac{1}{2} O_2\nearrow + H^{+},$$

$$\Delta G^{\circ\prime} = 52.1 \text{ kcal} \times \text{mole}^{-1} \text{ at pH} = 7$$

and, supplementary to the production of 2 ATP from:

$$ADP + PO_4H_2^{-} \overset{H_2O}{\xrightarrow{\nearrow}} ATP,$$
$$\Delta G^{\circ} \sim +7 \text{ kcal} \times \text{mole}^{-1} \text{ at pH} = 7$$

from 4 photons in the visible range of light frequencies, representing about 200 kcal, which implies an energetic yield of conversion of radiant energy to chemical energy, which is about 30%, i.e., far larger than that obtained from artificial photocells. As shown here, it now clearly appears that the general principles involved in plant photosynthesis do not require for being set in place efficiently all the sophistications which have been produced by evolution, to such an extent that the simulation of photosynthesis in artificial simpler systems would probably be the best way of converting solar energy into electrochemically useful energy in quite an efficient way.

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Semiconduction theory

by C. I. Simionescu and V. Percec

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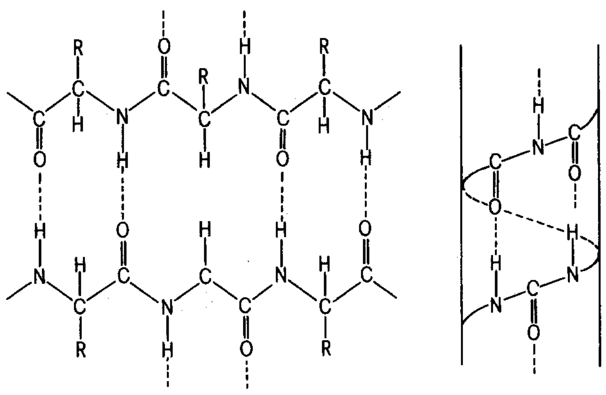
Szent-Györgyi suggested in 1941[1,2] that the application of the concepts of solid-state physics in biology could lead to a better understanding of certain biochemical processes. He proposed the existence of conduction bands in protein structures, producing in 1946 electrical conductivity of dry protein film as the first experimental evidence[3]. In 1949 Evans and Gergely[4] performed a simple molecular orbital calculation and demonstrated theoretically the existence of a banded structure in β-proteins (figure 1) as a consequence of electronic conjugation through the π orbitals of the =C=O ... H–N= hydrogen bridges.

During the following years the suppositions of Szent-Györgyi were confirmed, so that in 1967 Gutmann and Lyons[5] listed 116 biochemicals and organelles exhibiting semiconducting properties that had already been determined. Recently the semiconducting properties of biopolymers were reviewed by Eley[6], Rosenberg and Postow[7,8] and Simionescu et al.[9].

In the present paper, those notions of the semiconduction theory for biomacromolecules are presented (without going into detail) that are generally valid for


β-protein

α-protein

Fig. 1. The hydrogen bridge system in α- and β-proteins.