

Photosynthetic Oxygen Evolution

edited by
H. Metzner

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H. Metzner

*University of Tübingen
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PREFACE

In spite of intensive research some partial reactions of plant photosynthesis are still unknown. Whereas the path of carbon has been clearly elucidated meanwhile, the path of oxygen has still to be explained. There cannot be any doubt that the photosynthetic oxygen must be finally derived from water molecules. But the experimental data do not prove that there is a light-induced water decomposition ("photolysis").

There is general agreement that the photon energies absorbed by the sensitizer molecules can migrate within extended "antennae" before they reach a "reaction center". It is at these distinctive spots, where the first *chemical* reaction occurs. Apparently this primary step consists in an electron exchange between a donor - probably an excited sensitizer dimer - molecule and a still unidentified acceptor. Whereas the reduced acceptor handles its surplus negative charge *via* a chain of redox couples to the donor of a second light reaction, the oxidized primary donor has to regain its missing electron. To oxidize O^{2-} anions to the oxidation state of molecular oxygen, four electrons have to be removed. Under continuous illumination the "waiting time" for a chlorophyll molecule between two photon absorptions is by orders of magnitudes longer than the survival time of the excitation energy. So there must be a transformation of the excitation energy into some form of a long-living intermediate.

Experiments with periodic light flashes demonstrate that the antennae need *four* flashes to release *one* oxygen molecule. This favours the assumption of a charge accumulation mechanism. On the other hand, it has long been realized that the O_2 -releasing reaction requires the presence of organically bound manganese. Since this transition metal can exist in various oxidation states, there are many speculations on the natural Mn complex and on the possible mechanism by which it can store positive charges.

The next open question is the nature of the donor which reacts with the oxidized center. Here we have to regard experimental data on both oxygen and hydrogen isotope discrimination, which speak against the oxidative splitting of either free or bound water. Until now there is, however, no convincing alternative to the hypothesis

PREFACE

of H_2O decomposition.

Facing these problems, a Symposium on "Photosynthetic Oxygen Evolution" was invited to Tübingen. It was the intention of this meeting to present the meanwhile obtained data, to discuss their often controversial interpretations and to look for practicable new techniques to perform crucial experiments. To achieve this goal, photosynthesis specialists met with photo- and electrochemists and experts from other fields of physico-chemical research. This revealed the opportunity to recognize the present-day view on the structure of water and aqueous solutions, on the behaviour of irradiated redox systems and the properties of various model systems, including synthetic manganese complexes.

Most of the time was devoted to comparative studies on the light-induced charge exchange on the donor site of the photosynthetic electron transfer chain. These discussions included the proposal of new inhibitors and new aspects on the role of carbon dioxide. They also dealt with the structure of the photosynthetic apparatus and its ontogenetic evolution.

The success of the meeting encouraged the organizer to prepare all the contributions for printing. Publisher and editor expect that by this means they display the present state of knowledge and at the same time exhibit the most controversial problems. They do hope that the test will motivate biochemists, biophysicists and biologists to pursue a way which urgently asks for a close cooperation between different scientific disciplines.

The editor wants to thank all his colleagues, who agreed to have their contributions collected in a special volume. He extends his sincere gratitude to the sponsors of the Symposium - the Deutsche Forschungsgemeinschaft and the Ministry of Cultural Affairs of Baden-Württemberg - as well as to the coworkers of Academic Press Inc., London, both for retyping the manuscripts and for their effort to publish this volume at the earliest possible date.

Tübingen, September 1977

LIST OF ABBREVIATIONS

AAS	atomic absorption spectroscopy
ACC	anthraquinonecyanine
ANT 2s	2-(3,4,5-trichloro)-anilino-3,5-dinitrothiophene
BLM	bilayer lipid membrane
BQ	<i>p</i> -benzoquinone
Chl	chlorophyll
Ch _T	chlorophyll triplet
CL	continuous light
CP	chlorophyll-protein-complex
DBMIB	2,5-dibromo-3-methyl-6-isopropyl- <i>p</i> -benzoquinone
DCMU	3-(3,4-dichlorophenyl)-1,1-dimethylurea
DCPIP	2,6-dichlorophenol indophenol
DMP	dimethylphthalate
DNB	<i>m</i> -dinitrobenzene
2,4-DNP	2,4-dinitrophenol
DPC	2,5-diphenylcarbazine
EDTA	ethylenediamine tetraacetic acid
EPR	electron spin resonance
FCCP	carbonylcyanide- <i>p</i> -trifluoromethoxyphenylhydrazone
HEPES	N-2-hydroxyethyl-piperazine-N-2-ethanesulfonic acid
FeCy	potassium ferricyanide
HQ	hydroquinone
LDC	light-dark cycle
MA	methylamine
MES	morpholinoethan sulfonic acid
MP ⁺	N-methylphenazinium cation
MV	methylviologen
NMR	nuclear magnetic resonance
NphSH	<i>p</i> -nitrothiophenol
OEC	oxygen evolving complex
OES	oxygen evolving system
Pc	phthalocyanine
PCB ⁻	C-phenyl-1,2-dicarba-undecaborate
PhD	phenylene diamine
PMS	phenazinemethosulfate
PS	photosystem
PTFE	polytetrafluor-ethylene
Q	quencher (primary acceptor of photosystem II)
Q	quinone

LIST OF ABBREVIATIONS

R	secondary acceptor of photosystem II
5-SAL	N-oxyl-4,4-dimethyloxazolidine derivative of 5-keto-stearic acid
SCE	standard calomel electrode
SDS	sodium dodecyl phosphate
SOD	superoxide dismutase
T-A	TRIS-acetone washed chloroplast membranes
TAA	dihydro-dibenzo-tetraazaannulene
Th	thionine
Th _T	thionine triplet
TPB-	tetraphenylboron anion
TPP	tetraphenylporphyrine
Tricine	N-[tris(hydroxymethyl)-methyl]-glycine
TRIS	tris(hydroxymethyl)aminomethane
α	miss parameter
β	double hit parameter

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STRUCTURE OF WATER AND AQUEOUS SYSTEMS

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Non-polar liquids

In search of a model for the liquid state, the hole model is simple and explains many properties [28]. One can think of a solid-like packed state. It expands with temperature on behalf of thermic vibrations and in addition contains holes, the concentration of which equals the number of molecules in the vapour phase, with which it is in equilibrium. With this quite powerful model one can understand Raoult's law: if we add extraneous molecules to our model-liquid, they occupy the holes; if the solved molecules do not have any vapour pressure, the pressure over the solution falls proportional to the amount of added particles. This model essentially holds for non-polar substances and is useful to calculate quantitatively the properties of non-polar liquids like heat of vapourization, specific heat or surface energy and surface tension [28]. To do this one needs an estimation of the intermolecular pair-potential. This can be taken from $3/2 R \cdot T_c$ (T_c = critical temperature). This calculation can be done with liquid CH_4 ; its result is in reasonable agreement with the experimental heat content (H). If we compare the curves for methane and water (Fig. 1), which have comparable molecular weights, we observe large differences. Ice has a heat of sublimation of $\sim -48.6 \text{ kJ} \cdot \text{mol}^{-1}$ ($= -11.6 \text{ kcal} \cdot \text{mol}^{-1}$). The heat of melting is

$\sim -5.9 \text{ kJ}\cdot\text{mol}^{-1}$ ($\sim -1.4 \text{ kcal}\cdot\text{mol}^{-1}$). With further rise of the temperature the heat content gradually increases to comparatively high values. If we vapourize water at the melting point we need approximately $42 \text{ kJ}\cdot\text{mol}^{-1}$ ($\sim 10 \text{ kcal}\cdot\text{mol}^{-1}$). We see, that the intermolecular interaction, which this plot describes in principal, is much higher with water than with methane. The reason for this totally different behaviour of water and all liquids with OH groups lies in the strong and angle-dependent intermolecular forces between protons and lone pair electrons of oxygen atoms. The angle can be easily understood, if we look at the model of a H_2O molecule. We have two

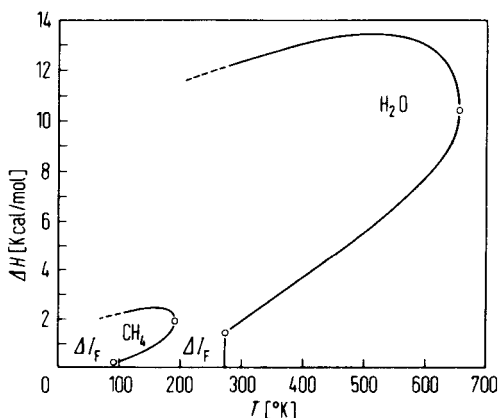


Fig. 1. Comparison of the heat content of methane and water.

positive centres at the protons and two negatively charged lone pair electrons; the connecting lines of these four charged spaces with the central oxygen closely form the angle of the tetrahedron. One can easily imagine, that the interaction with a second H_2O molecule very much depends on their relative orientation: if a proton approaches a lone pair electron attraction results, if a proton approaches another proton, the result will be repulsion, already at relative large distances. This phenomenon is not found with non-polar liquids. On behalf of this 3-

dimensional angle-dependent interaction we better understand the anomalous properties of water. Comparing water and methane we see, that water should boil at -80°C if it would not have any H bond interaction. Thus hydrogen bonds are fundamental for the water structure and the reason why we find living organisms on our planet.

As already mentioned, the interaction of H_2O molecules is angle-dependent and in the case of the approach of a proton and a lone pair electron - i.e. at H bond formation - it is maximal if the angle between the O-H bond-axis and the lone pair electron orbital is zero. If we fix H_2O molecules at this angle - the direction of lone orbitals may be symbolized by holes and that of the proton axis by a pin - we get the ice structure; it has a loose packing with four next neighbours contrary to non-polar substances, which may be regarded as a closest packing of spheres with about 12 first next neighbours. In ice we have six-membered rings of H bonded molecules, which are very stable. They give rise to the tridymite structure, which in certain directions has hexagonal symmetry. This finds a direct equivalent in the hexagonal symmetry of ice crystals grown under equilibrium conditions [17].

Structure of liquid water

Different from non-polar liquids orientation defects have to be taken into account in the liquid state of water. That means, that some of the hydrogen-bonds are opened - as given by the BOLTZMANN partition of energy - and the strong interaction (which totals approximately 17 kJ per H-bond) is reduced. So we can describe the liquid structure of water, if we are able to determine the amount of these orientational defects. This is possible by the use of infrared spectroscopy, especially in the overtone region [21, 26]. Fig. 2 gives the spectrum of HOD. For spectroscopic reasons partially deuterated water, which has the same liquid structure as normal water, is used.