Self-Organization of Water Molecules Over 11-Year Solar Cycle

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SELF-ORGANIZATION OF WATER MOLECULES OVER 11-YEAR SOLAR CYCLE

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The variations of solar activity and distribution of solar energy due to the rotation of the Earth around its axis and around the Sun exert a strong influence on the self-organization of water molecules. As a result, the rate of hydrolytic processes with the participation of water clusters displays diurnal, very large annual variations, and is also modulated by the 11-year cycles of solar activity. It also depends on the geographic latitude and can be different at the same time in the Northern and Southern Hemispheres.

This phenomenon is well accounted for by the influence of muons on the self-organization of water molecules. Muons are constantly generated in the upper atmosphere by the solar wind. They reach the surface of the Earth and can penetrate to some depth underground. Buildings also absorb muons. For this reason, the rate of hydrolysis outside and inside buildings, as well as underground, can differ significantly from each other.

Introduction

Water possesses unique properties owing to the ability of its molecules to form hydrogen bonds with each other. In the bulk phase all water molecules form a common continuous three-dimensional network of hydrogen bonds in which every molecule has tetrahedral bonding directions.^{1,2} However, on mixing water with organic solvents, for example, with acetonitrile, this network disintegrates with the formation of clusters $(\text{H}_2\text{O})_n$ rather than single water molecules. The size of clusters may vary from a few water molecules to several hundreds.³ In large clusters hydroxyl groups ($-\text{OH}$) are involved in the network of hydrogen bonds, whereas small clusters, especially of the size $n < 6$, contain a lot of free $-\text{OH}$ groups, since they are unable to form three-dimensional structures.^{1,2,4-6} For this reason small clusters are chemically more reactive than large

ones, and the same solution of water in acetonitrile can have different hydrolytic activity as it can consist of a small number of big clusters or a large number of small clusters.

We have found that variations of solar activity and distribution of solar energy due to the rotation of the Earth around its axis and around the Sun exert a strong influence on the self-organization of water molecules in clusters, as a result of which the hydrolytic activity of the same solution of water in acetonitrile can vary in a very wide range. To detect this influence experimentally and to determine the chemical reactivity of water clusters quantitatively proved possible by means of hydrolysis of phosphoric acid esters, for example, triethylphosphite **1**. (Figure 1) This compound possesses special properties. After hydrolytic cleavage of P-O bond the three-coordinate phosphorus atom immediately rearranges into tetra-coordinate diethylphosphonate **2**, which is not acidic and does not destroy water clusters. The presence of phosphorus atom is also a necessary condition, as it allows determining the conversion rate quickly and accurately by ^{31}P -NMR-spectroscopy at any stage of the reaction without stopping it.

Figure 1. Hydrolysis of triethylphosphite **1** into diethylphosphonate **2**. ^{31}P -NMR spectrum displays two signals at +140 ppm and +9 ppm respectively. Measuring the integral intensities of these signals allows determining the conversion rate.

Regular measurements of the rate of hydrolysis of triethylphosphite in acetonitrile were started in 2015. (Figure 2) It was found, that this reaction does not obey the law of chemical

thermodynamics. When the temperature, concentration and other conditions remain unchanged, the rate of this reaction is highly unstable and displays diurnal, very large annual variations, and is also modulated by 11-year cycles of solar activity. This was shown by regular measurements during 6 years 2015-2020. This period includes the second half of the 24-th solar cycle 2015-2019 and the first year of the 25-th cycle (Figure 2).

Figure 2. Variations of the rate of hydrolysis of triethylphosphite in acetonitrile in the second half of the 24-th solar cycle (2015-2019) and in the first year of the 25-th cycle (2020). Conversion after 25 minutes of heating at 80°C.

61 The diurnal variations are accounted for by the change of the Sun influence because of the
62 rotation of the Earth around its axis. In the morning the reaction rate is usually lower and rises by
63 noon (up to 2-4 times), and then it slows down again. However, this order may sometimes be
64 violated by sharp short-term changes in solar activity. The range of diurnal changes is not constant
65 either and can vary on different days throughout the year. In periods of low solar activity the diurnal
66 variations become less pronounced.

67 One more important conclusion is that this reaction is highly unstable and demonstrates also
68 very large annual rate variations because of the rotation of the Earth around the Sun. (Figure 2)
69 Every year the reaction slows down in winter and accelerates in summer. In January 2015 the
70 reaction was slow and accelerated twice in February. In March the rate slowed down again and
71 then, in April it started to grow gradually. At the end of June a sharp rise occurred and in early July
72 the reaction rate was record-breaking. At the end of August, the reaction slowed down rapidly
73 within two weeks back to the April level. From September till the end of the year the average
74 reaction rate declined gradually 2 times more. In December the rate did not return to the level of the
75 beginning of the year and exceeded it about 2-3 times.

76 Thus, in 2015 the rate of hydrolysis of triethylphosphite in acetonitrile at 80°C changed
77 within a very wide range, the difference between single experiments in January and in July reaching
78 50 times. The reaction being conducted at room temperature, this seasonal difference was even
79 more significant. For example, in July 2015 the reaction at 20°C was completed in 10-15 minutes,
80 whereas in January the same reaction mixture could react 2 days, which is 200 times slower. The
81 smaller seasonal rate difference at 80°C is accounted for by an increase in chemical reactivity of
82 water clusters because of their destruction at more high temperature. It is well confirmed
83 experimentally. For example, triethylphosphite hydrolyses at 20°C substantially faster if a solution
84 of water in acetonitrile was preheated at 80°C before the reaction.

85 Further measurements showed that the annual variations in the rate of this reaction are
86 different each year and correlate with the variations in solar activity during the 11-year solar cycle.

87 In 2016 a significant summer acceleration of this reaction took place again. It lasted till the
88 end of July. However, in this year the acceleration was very intensive already in April and May.
89 This coincides with the temperature observations of NASA Goddard Institute for Space Studies,
90 according to which April and May 2016 set new global temperature records for those two months.⁷
91 In the second part of September one more acceleration of a shorter duration and smaller intensity
92 took place. (Figure 2) In 2016 the diurnal rate variations were also constantly observed. Every day
93 the reaction accelerated towards noon and then it gradually slowed down.

94 In 2017 the rate of this reaction continued to remain very dynamic, however, a noticeable
95 lowering of activity was observed. The annual difference between winter and summer rates became
96 less pronounced. That year another interesting evidence of solar influence on water clusters was
97 experimentally observed. On August 21 a solar eclipse took place, immediately after which the rate
98 of hydrolysis of triethylphosphite decreased sharply. Especially strong slowing down (8-10 times)
99 was registered when the reaction was conducted at 20°C. The deactivated state lasted 5 days, after
100 which the rate returned to the previous level.

101 In 2018 the slowing down of the reaction became especially strong and by the end of the
102 year the reaction rate decelerated unprecedentedly. Against the background of low rate, four times
103 in 2018 (June 2, July 29, November 8 and December 3) extremely sharp accelerations of short
104 duration took place. During 4-6 days the rate gradually relaxed to the original value. On November
105 8 and December 3 this occurred at the moment of conducting measurements, which allowed to
106 determine that the reaction rate increased (more than 20 times) within several minutes. Such sharp
107 acceleration with the following relaxation of the rate points to the fact that it can be caused by
108 external factors only.

109 In September 2018 studies were simultaneously conducted in Stuttgart, 1500km away from
110 Kiev. In both places the diurnal deviations were distinctly observed, which confirms the solar
111 influence on the rate of this reaction and excludes the influence of any local factors. The average
112 rate in Stuttgart was constantly about 2 times higher than in Kiev, which can be accounted for by
113 the difference in geographic latitude.

In 2019 a further decrease in the rate of hydrolysis was observed. Similarly to the previous years the summer acceleration took place, however, it was much less pronounced and strong sharp accelerations were absent. At the end of the year, in November and December, like the year before the reaction became very slow, with one insignificant short acceleration taking place in December.

Thus, regular measurements over 5 years (from January 2015 to December 2019) showed that the rate of hydrolysis of triethylphosphite in acetonitrile *ceteris paribus* displays diurnal variations and varies within very wide ranges throughout one year because of the rotation of the Earth around its axis and around the Sun respectively. However, as can be seen from Figure 2 the annual rate changes are different every year and from 2015 to 2019 a general gradual deceleration of the reaction took place. This deceleration is in good agreement with the decline in solar activity in the 24-th 11-year cycle which started in December 2008 and ended in December 2019.

Observations of solar activity from Wolf spots show that the decrease in activity from maximum to minimum over about 5.5 years does not occur uniformly, but it occurs more rapidly in the last three years of the solar cycle. The same dynamics manifested itself in the rate of hydrolysis of triethylphosphite from 2015 to 2019. In 2015-2016, with high solar activity, an extremely high summer rate was observed, and in the last three years (2017-2019) it decreased to a minimum.

In December 2019 the 24th solar cycle ended and a new 25th cycle began. Long-term investigations of 11-year cycles show that the rise in solar activity at the beginning of the cycle is noticeably faster than the decline in activity at the end of the cycle. This was also observed in 2020 in the hydrolysis of triethylphosphite. (Figure 2) In the first 5 months of the new 11-year cycle, until May 2020, the rate of this reaction remained very low. However, at the end of June, exactly as in 2015, there was a sharp strong acceleration and till the end of the year the rate remained much higher, than in the previous year. For example, in December 2020 it was 10 times higher than in December 2019 or in December 2018.

140 DISCUSSION

141 Mechanism

142 Thus, 6-year investigations from 2015 to 2020 show that self-organization of water
143 molecules and chemical reactivity of water clusters are extremely sensitive to the variations in solar
144 activity over the 11-year solar cycle. Solar irradiance at short wavelengths and solar wind are highly
145 dynamic and vary by as much as an order of magnitude on time scales of minutes to hours (solar
146 flares), days to months (solar rotation), and years to decades (solar cycle).⁸ The observed variations
147 in the rate of hydrolysis are well explained by the influence of muons. These particles are constantly
148 generated in the upper atmosphere by the solar wind and cosmic rays and their amount is also
149 modulated by the solar activity. In contrast to the solar wind particles muons reach the surface of
150 the Earth and can penetrate to some depth underground.

151 The intensity of the muon flux displays diurnal and annual variations, the same as the rate of
152 hydrolysis of triethylphosphite. During the day the muon flux reaches its maximum at noon, when
153 the Sun is at its zenith, and the annual increase occurs in summer. It has been recently discovered
154 that the formation of muons can sharply increase at the end of June.^{9,10} Exactly at that time the
155 sharp acceleration of the rate of hydrolysis of triethylphosphite in 2015, 2016 and 2020 was
156 observed. One more confirmation of the fact that muons destroy water clusters and thus accelerate
157 hydrolytic processes was obtained by conducting experiments underground, where this effect
158 should either disappear or slow down significantly, due to the weakening of the muon flux. In
159 several control experiments at the depth of 105 meters triethylphosphite hydrolyzed 4 times slower
160 than inside the Institute and 8-10 times slower than outside of it. It is important to note that the
161 diurnal variations underground and on the surface were the same. The reaction accelerated towards
162 noon and then slowed down again.

163 An interesting evidence of the influence of muons on the hydrolysis of triethylphosphite was
164 also found in the fact, that by means of this reaction the anisotropy of the muon flow can be
165 observed. We found that the same reaction mixtures prepared in different parts of a large building
166 react at different rates depending on the direction of the muon flux. This difference depends also on

the position of the Sun in the sky and changes during the day. This phenomenon is explained by the absorption of muons by building structures and is clearly observed in summer during periods of high solar activity. For example, on the roof and in the basement of a big building the difference in the rate of hydrolysis can be large. The absorption of muons by civil structures as well as mountains and volcanoes has already been registered by physical methods. The best known example is the investigation of one of the Egyptian pyramids by muons.¹¹

Dependence on geographic latitude

The measurements of the rate of hydrolysis of triethylphosphite were conducted in the Northern Hemisphere, in Kiev at 50 degrees North latitude. Every year the rate of this reaction increases from winter to summer and reaches its maximum at the end of June shortly after the summer solstice. At this time the maximum number of muons is formed, which destroy water clusters and increase their chemical reactivity.

However, in the Southern Hemisphere, the end of June is the time of the winter solstice, when solar influence becomes minimal and the amount of muons decreases. Under such conditions water molecules form big, stable, chemically inactive clusters and the rate of hydrolytic reactions is decelerated. This means that simultaneously in the Northern and Southern Hemispheres the hydrolysis of triethylphosphite should have different rates. In June and December this difference at 20°C may be very large, and during the spring and autumn equinoxes it should decrease.

Thus, self-organization of water molecules and chemical reactivity of water clusters depend not only on the solar activity and the position of the Earth relative to the Sun, but also on the geographic latitude. One more conclusion is that solar influence on water molecules may also depend on the Interplanetary Magnetic Field, since the particles of the solar wind and muons have an electric charge.

The opposite influence of the Sun on the self-organization of water molecules in the Northern and Southern Hemispheres can be compared with the Northern and Southern Lights. Both of these phenomena depend on the latitude and position of the Earth relative to the Sun, and the Solar Wind is their common course. The difference is that the solar wind influences water on the

Earth's surface through muons, and the polar lights are formed under its direct influence in the magnetosphere and upper atmosphere.

Influence of salts

In the presence of salts the self-organization of water molecules and formation of water clusters are substantially facilitated. Therefore, even a small amount of salts dissolved in water noticeably slows down the hydrolysis of triethylphosphite. All presented results were obtained using fresh water from the Dnieper. With distilled water, hydrolysis is accelerated by 1,5-2 times, and an increase in amount of salts greatly slows down the reaction. For example, with the Dead Sea water, even in summer, the process at 20°C can last more than one week, that is about 500 times longer than with water from the Dnieper. This proves that the optimal amount of salts in water is necessary for life on the Earth.

Biological rhythms

The hydrolytic cleavage of phosphorus-oxygen bond in triethylphosphite can be considered as a simplified model system of the conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) which is known to underlie bioenergetic processes in living organisms.^{12,13} The dependence of biochemical processes on solar activity during the rotation of the Earth around the Sun is well known as circannual rhythms, which are also not the same every year.¹⁴ For example, owing to the 11-year cycles of solar activity, annual growth rings in trees have different thickness and are arranged in 11-year sequences.¹⁵ This proves that the conditions for biochemical processes are different each year and are modulated by the 11-year cycles of solar activity.

In all forms of life (in plants, animals, fungi and bacteria) the so called circadian rhythms, which are 24-hours oscillations of biological processes, are also widely observed.¹³ Since water is a necessary constituent in all forms of life, one can suppose that the discovered diurnal, annual and 11-year variations of water clusters reactivity underlie the circadian, circannual and 11-year biological rhythms.

CONCLUSION

Thus, the self-organization of water molecules, the stability of water clusters and their chemical reactivity are extremely sensitive to extraterrestrial influence associated with the 11-year cycles of solar activity. This influence has a complex mediated mechanism which includes the influence of muons on water clusters.

The rate of hydrolytic processes on the Earth depends on the geographic latitude and should be different at the same time in the Northern and Southern Hemispheres, because of different distribution of solar energy between them. Therefore, measurements of the rate of hydrolysis of triethylphosphite in different places can provide important information about the influence of space weather on the Earth, and at the equator where there should be no seasonal differences, such measurements may become an independent method for assessing solar activity. The discovered phenomenon is important for physical, chemical and biological research.

METHODS

Triethylphosphite was distilled before use. Acetonitrile was commercial and contained 0.01% of water. ^{31}P -NMR spectra were recorded with Varian Gemini 400 MHz and JEOL FX-90Q spectrometers. The $\delta^{31}\text{P}$ chemical shifts are referenced to 85% aqueous H_3PO_4 .

In a 20 ml glass vial (diameter 27 mm) protected from light fresh water (7 mg) was added to acetonitrile (400 mg). In 5 minutes triethylphosphite (30 mg) was added under nitrogen, the vial was sealed and placed on a hotplate protected from light. After 25 minutes of heating at 80°C the vial was quickly cooled in cold water, the reaction mixture was transferred to a 5mm-NMR tube and the ^{31}P -NMR spectrum was recorded.

For conducting experiments at room temperature the reaction mixtures were prepared in 5mm-NMR-tubes protected from light. The conversion was determined by measuring the integral intensities of the signals of triethylphosphite (chemical shift 140 ppm) and diethylphosphonate (9 ppm) in ^{31}P -NMR spectra.

All data generated or analyzed during this study are included in this published article.

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