INFLUENCE OF SOLAR ACTIVITY ON WATER CLUSTERS

ANNUAL VARIATIONS 2015-2019

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Dedicated to Alexander von Humboldt on the occasion of 250-th anniversary

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 water clusters, as a result of which their chemical reactivity in hydrolytic processes can vary in a very wide range. This phenomenon is well manifested in the hydrolysis of the phosphoric acid esters. 5-Year regular investigations (2015-2019) of the hydrolysis of triethylphosphite in acetonitrile show that the rate of this reaction with all other conditions being equal displays diurnal and annual variations, and is also modulated by the 11-year cycles of solar activity. The results obtained also point to the fact that the rate of this reaction should depend on the geographic latitude, and at the equator, where there should be no seasonal differences, measurements of the rate of this reaction may become an independent method for assessing solar activity.

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 large and small clusters should possess different

chemical reactivity, and the rate of hydrolytic processes with the participation of water clusters should depend on their size.

We have found that variations of solar activity exert a strong influence on the organization of water molecules in clusters, as a result of which the hydrolytic activity of the same solution of water in acetonitrile can vary within a very wide range in the course of hours, days, months and years. 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 (Figure 1) were started in 2015. It was found, that this reaction does not obey the law of chemical

thermodynamics. At constant temperature, concentration and other conditions being equal the rate of this reaction is highly dynamic and varies throughout the year over a very wide range. (Figure 2)

In January 2015 the reaction was very slow and accelerated twice in February. In March it slowed down again and then, in April it started to grow gradually till the middle of June. At the end of June a sharp rise occurred, after which a very high rate was established. It lasted two months till the end of August and then slowed down rapidly within two weeks back to the April level. From September till the end of the year the average reaction rate declined gradually 2 times more. It is remarkable that in December the rate did not return to the level of the beginning of the year and exceeded it about 2-3 times.

Figure 2. Fluctuation of the rate of hydrolysis of triethylphosphite in acetonitrile in 2015 (conversion into diethylphosphonate after 25 minutes of heating at 80°C).

Thus, the rate of hydrolysis of triethylphosphite in acetonitrile at 80°C changed in 2015 within a very wide range, the difference between single experiments in January and in July reaching 50 times. Simultaneously the experiments were also conducted at room temperature. The character of annual deviations of the reaction rate at 80°C and at room temperature was the same. However,

the amplitude of changes at low temperature was more significant. For example, in July the reaction was completed in 10-15 minutes, whereas in January the same reaction mixture could react 2 days, which is 200 times slower.

The decrease in the sensitivity of the hydrolysis rate at 80°C to the influence of solar activity is accounted for by the destruction of water clusters and an increase in their chemical reactivity. It is well confirmed experimentally. For example, triethylphosphite hydrolyses at 20°C substantially faster if a solution of water in acetonitrile was preheated at 80°C before the reaction.

Such considerable annual alteration of the reaction rate should be connected with the rotation of Earth around the Sun. One more important conclusion is that this reaction is in constant dynamics and also demonstrates diurnal variations because of the rotation of Earth around its axis. These variations are not chaotic. In the morning the rate is usually lower and rises by noon (up to 2-3 times) and then it slows down again. However, this order may sometimes be violated by sharp short-term changes in solar activity. The range of diurnal changes is not constant either and varies on different days throughout the year. In the periods of low reaction rate the diurnal difference decreases considerably.

Diurnal and annual rate variations of this reaction because of the rotation of Earth around its axis and around the Sun unambiguously point to the influence of solar energy. This was confirmed by further regular observations. In 2016 the general character of rate deviations of this reaction was like in the previous year. (Figure 3) At the beginning of 2016 the reaction rate was small then it accelerated considerably towards summer and slowed down again by the end of the year. However, noticeable differences manifested themselves as well. A sharp acceleration of the rate occurred almost 4 months earlier – not at the end of June, but at the beginning of March. The period of high activity lasted 2 months longer, till the end of July, after which the rate decreased rather sharply. In the second part of September another acceleration occurred, however of a shorter duration and smaller intensity.

Figure 3. Fluctuation of the rate of hydrolysis of triethylphosphite in acetonitrile in 2016 (conversion after 25 minutes of heating at 80°C).

In 2017 a noticeable lowering of activity of this reaction was observed. The annual difference between “winter” and “summer” rates became considerably less pronounced. However, the reaction continued to remain very dynamic. (Figure 4) That year another interesting evidence of the influence of solar energy on water clusters was experimentally observed. On August 21 solar eclipse took place, immediately after which the rate of hydrolysis of triethylphosphite decreased sharply. Especially strong slowing down (8-10 times) was registered in reactions at 20°C. The deactivated state lasted 6 days, after which the rate increased till the previous level.

Figure 4. Fluctuation of the rate of hydrolysis of triethylphosphite in acetonitrile in 2017 (conversion after 25 minutes of heating at 80°C).

In 2018 the slowing down of the reaction became especially strong. (Figure 5) In the first half of the year the reaction continued to remain very dynamic, but after August deviations became insignificant and disappeared by the end of the year. In November and December the reaction rate became unprecedentedly low. Against the background of low rate, four times in 2018 (June 2, July 29, November 8 and December 3) extremely sharp accelerations of short duration took place. During 4-6 days the rate gradually relaxed to the original value. On November 8 and December 3 this occurred at the moment of conducting measurements, which allowed to determine that the reaction rate increased (more than 20 times) within several minutes. Such sharp acceleration with the following relaxation of the rate points to the fact, that it can be caused by external factors only, like, for example, solar flare or coronal mass ejection.

Figure 6. Fluctuation of the rate of hydrolysis of triethylphosphite in acetonitrile in 2019 (conversion after 25 minutes of heating at 80°C).

Thus, regular measurements over 5 years (from January 2015 to January 2020) showed that the rate of hydrolysis of triethylphosphite in acetonitrile *ceteris paribus* can display diurnal variations and can vary 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 Figures 2-6 the picture of annual rate changes is different every year. Moreover, from 2015 to 2020 a general deceleration of the reaction took place. This deceleration is in good agreement with the decline in solar activity in the current 24-th 11-year cycle which started in December 2008.

The change in solar activity between the maximum and minimum over approximately 5.5 years does not occur evenly, but decreases quite sharply in the middle of this period. The same dynamics was observed in the rate of hydrolysis from 2015 to 2020. In 2015-2016 with high solar activity an extremely high summer rate was reproduced twice, and already one year later, in 2018-2019 an extremely low winter rate was observed two years in a row.

Thus, self-organization of water molecules and the stability of water clusters are extremely sensitive to the variations in solar activity. Solar energy reaches the Earth in the form of electromagnetic radiation and in the form of solar wind – a stream of charged particles, mostly electrons, protons and alpha particles. Solar irradiance at short wavelengths, the solar wind speed and its density are highly dynamic and vary by as much as an order of magnitude on time scales of minutes to hours (solar flares), days to months (solar rotation), and years to decades (solar cycle).⁷

We have found that ultraviolet radiation decomposes water clusters and accelerates the hydrolysis of triethylphosphite in acetonitrile very strongly. However, the solar ultraviolet radiation cannot exert such influence, as it is adsorbed by the atmosphere of the Earth. For the same reason the particles of solar wind cannot reach the surface of the planet either. But they are known to be able to produce other active particles in the upper atmosphere – muons, which can even penetrate under the ground. It is logical to assume, that if any particles, for example muons, destroy water clusters and thus accelerate hydrolytic processes, then this effect should either disappear or slow down significantly underground. This supposition was confirmed by several experiments carried out at the depth of 105 meters. Underground triethylphosphite hydrolyzed about 4 times slower. It is important to note that the diurnal variations in the reaction rate were exactly the same as on the surface.

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 bioenergetics processes in living organisms.^{8,9} 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.¹⁰ 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.¹¹ 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.⁹ Taking into

account that water is a necessary constituent in all forms of life, one can suppose that the diurnal and annual variations of water clusters reactivity discovered may underlie the circadian and circannual 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 variations of solar activity. This influence obviously has a complex mediated mechanism and requires detailed study.

The significant annual change in the chemical reactivity of water clusters due to the Earth's rotation around the Sun means that the rate of hydrolysis of triethylphosphite should depend on the geographic latitude and, therefore, 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 this reaction 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.

METHODS

Triethylphosphite was distilled before use. Acetonitrile was commercial and contained 0.01% of water. All experiments were conducted in darkness. ^{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 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. 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. 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. Experiments were conducted with fresh water and with distilled water and displayed the same hydrolysis rate variations. However, it should be noted that triethylphosphite hydrolyzes with distilled water somewhat faster (about 50%) than with fresh water. All data generated or analyzed during this study are included in this published article.

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