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## **Influence of the solar energy on the self-organization of water molecules. Diurnal, annual, and 11-year variations**

*Presented by Corresponding member of the NAS of Ukraine O.I. Kolodyazhnyi*

*Solar energy exerts a strong influence on the ability of water molecules to the self-organization. This influence is manifested on the chemical reactivity of water clusters. The rate of hydrolytic reactions involving water clusters can vary within very large limits over the course of minutes, hours, days, months, and years. The results of regular 4-year (2015-2018) investigations of the hydrolysis of triethylphosphite in acetonitrile indicate that the rate of this reaction with all other conditions being equal displays diurnal and annual variations and may be also modulated by the 11-year cycles of solar activity. The hydrolytic cleavage of a 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. The dependence of biochemical processes on the solar activity during the rotation of the Earth around its axis and around the Sun is well known in all forms of life (in plants, animals, fungi, and bacteria) as circadian and circannual rhythms. For example, owing to the 11-year cycles of solar activity, the annual growth rings in trees have different thicknesses and are arranged in 11-year sequences. Taking into account that water is a necessary constituent in all forms of life, one can suppose that the discovered diurnal and annual variations of the water reactivity may underlie the circadian and circannual rhythms.*

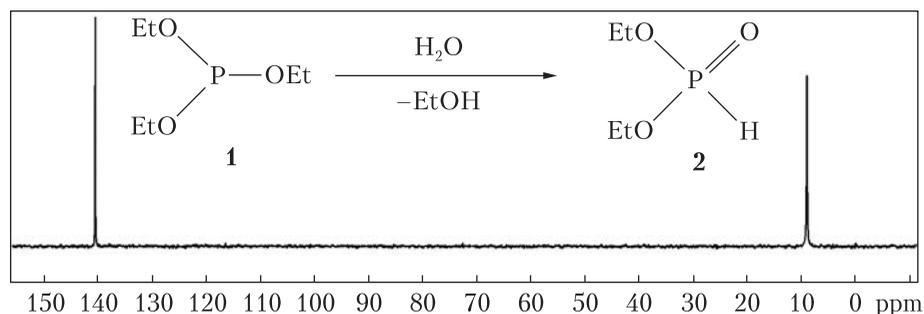
**Keywords:** *solar energy, hydrolysis, water clusters, circadian rhythms, circannual rhythms, 11-year cycles.*

It has been recently found that, at constant temperature, concentration, and other conditions being equal, the rate of hydrolysis of triethylphosphite in acetonitrile (Fig. 1) is highly dynamic and varies throughout the year over a very wide range [1]. This was shown by regular measurements started in 2015 (Fig. 2).

In January, the reaction was very slow and accelerated twice in February. In March, it slowed down again. 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, after the autumnal equinox 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.

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

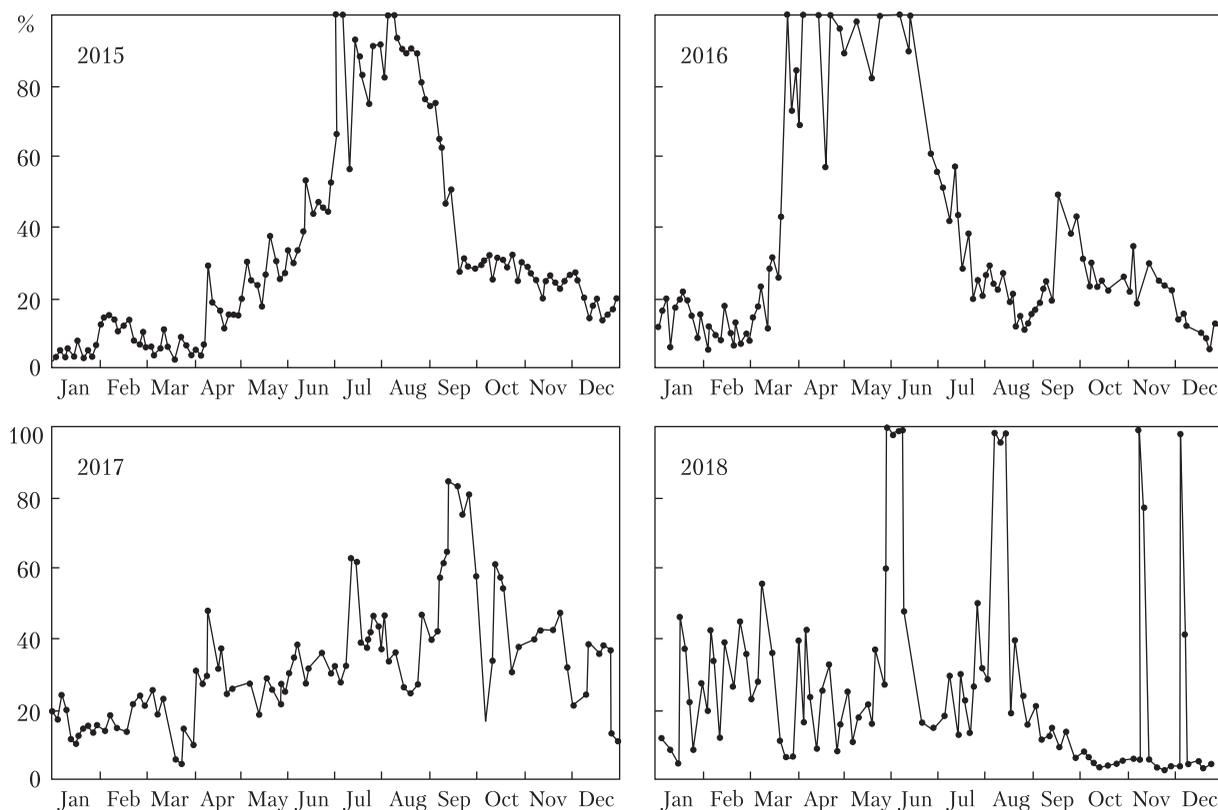
Thus, the rate of hydrolysis of triethylphosphite in acetonitrile at 80 °C changed in 2015 within a very large range, the difference between single experiments in January and in July reaching 50 times. Simultaneously, the experiments were also conducted at room temperature. The character of annual deviations of the reaction rate at 80 °C and at room temperature was the same. However, the amplitude of changes at the low temperature was even more significant. For example, the reaction in July was completed in 10-15 minutes, whereas the same reaction mixture could react 2 days in January.

Such considerable annual alteration of the reaction rate should be connected with the rotation of the Earth around the Sun. This means that the rate of this reaction should be dependent on the geographic latitude and can considerably differ at the same time in north and south hemispheres, because of different distributions of the solar energy between them.

One more important conclusion is that this reaction is in constant dynamics and also demonstrates diurnal variations because of the rotation of the Earth around its axis. These variations are not chaotic. In the morning, the rate is usually lower and rises in the day time, and then it slows down again. The range of diurnal changes can reach 4-5 times. However, it is not constant and varies on different days throughout the year. In the periods of low solar activity, the reaction rate decreases, and the diurnal variations become insignificant.

Diurnal and annual rate variations of this reaction because of the rotation of the Earth around its axis and around the Sun unambiguously point to the influence of the solar energy. Solar irradiance at short wavelengths, like the Extreme Ultraviolet (EUV), is highly dynamic and varies 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). The space weather impacts are also highly dependent on the solar wind speed, solar wind density, and the direction of the magnetic field embedded in the solar wind [2].

The annual alterations of the reaction rate were confirmed by further observations. In 2016, the general character of rate deviations of this reaction was like in the previous year (see Fig. 2). At the beginning of 2016, the reaction rate was relatively 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



**Fig. 2.** Fluctuation of the rate of hydrolysis of triethylphosphite in acetonitrile in 2015, 2016, 2017, and 2018 (conversion after 25 min of the heating at 80 °C)

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, it had a shorter duration and smaller intensity.

In 2017, a noticeable lowering of the activity of this reaction was observed. The annual difference between the “winter” and “summer” rates became considerably less pronounced. However, the reaction continued to remain dynamic (see Fig. 2).

In 2018, the slowing down of the reaction became especially strong (see Fig. 2). 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. Against the background of a very low rate, the extremely sharp accelerations of a short duration took place four times in 2018 (June 2, July 29, November 8, and December 3). 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 us 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 a solar flare or the coronal mass ejection.

The dependence of the rate of this reaction on the extraterrestrial influence was confirmed in September 2018 by conducting simultaneous measurements in Stuttgart and in Kiev. In both

places, the diurnal deviations were distinctly observed. The average rate in Stuttgart was constantly approximately 2.5 times higher than in Kiev.

Thus, the regular measurements over 4 years showed that the rate of hydrolysis of triethylphosphite in acetonitrile *ceteris paribus* can vary within very wide ranges throughout one year. However, as can be seen from Fig. 2, the picture of rate changes is different every year. Moreover, from 2016 to 2018, a general deceleration of the reaction took place. This deceleration correlates with a decrease of the solar activity in the course of the current 24-th 11-year cycle which started in December 2008. The solar activity is evaluated by the number of Sun spots and expressed in Wolf numbers. In 2014, the annual Wolf number reached maximum (121.8) and then gradually reduced to a minimum (6.5) in 2018.

The hydrolytic cleavage of a 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 [3, 4]. The dependence of biochemical processes on the 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 [5]. For example, owing to the 11-year cycles of solar activity, the annual growth rings in trees have different thicknesses and are arranged in 11-year sequences [6]. 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-hour oscillations of biological processes, are also widely observed [5]. Taking into account that water is a necessary constituent in all forms of life, one can suppose that the diurnal and annual variations of the water reactivity discovered may underlie the circadian and circannual rhythms.

The change of the rate of hydrolysis of triethylphosphite is well accounted for by the ability of water molecules to form clusters  $(H_2O)_n$ . 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 [7, 8]. However, on mixing water with acetonitrile, this network disintegrates with the formation of clusters [9]. The chemical reactivity of water clusters depends on their size, which may vary in a wide range – from a few water molecules to several hundreds. Large clusters contain fewer free hydroxyl groups ( $-OH$ ), which are not involved in the network of hydrogen bonds, which reduces their chemical reactivity, whereas the clusters of the size  $n < 6$  are especially reactive, since they are unable to form three-dimensional structures [7, 8, 10-12].

The size of water clusters and therefore their chemical reactivity are greatly influenced by various physical factors. For example, with an increase of the temperature the clusters decompose and become more reactive. That is why after cooling the heated reaction solution from 80 °C to 20 °C, the reaction rate decreases only about 5 times rather than 64 times according to the law of chemical thermodynamics. Light also decomposes clusters and accelerates the hydrolysis of triethylphosphite in acetonitrile. Particularly strong is the influence of ultraviolet radiation [13]. The rate of hydrolysis of triethylphosphite in acetonitrile is also affected by the electric field which can both speed up and slow down the reaction at different times of the year [1].

Thus, the self-organization of water molecules and their chemical reactivity are extremely sensitive to the extraterrestrial influence associated with variations of the solar energy. This influence obviously has a complex mediated mechanism and requires detailed study.

**Materials and Methods.** Triethylphosphite was distilled before use. Acetonitrile was commercial and contained 0.01 % of water. All experiments were conducted in darkness.  $^{31}\text{P}$ -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  $\text{H}_3\text{PO}_4$ .

In a 20-ml glass vial (diameter 27 mm), triethylphosphite (30 mg) was added under nitrogen to a freshly prepared solution of water (7 mg) in acetonitrile (400 mg). The vial was sealed and placed on a hotplate. When water was mixed with acetonitrile and during the reaction, the samples were shielded from light. After 25 min of the heating at 80 °C, the vial was quickly cooled to 0 °C, the reaction mixture was transferred to a 5mm-NMR tube, and the  $^{31}\text{P}$ -NMR spectrum was recorded. The conversion was determined by measuring the integral intensities of the signals of triethylphosphite (chemical shift 140 ppm) and diethylphosphonate (9 ppm) in  $^{31}\text{P}$ -NMR spectra.

Experiments were conducted with distilled water and with fresh water and gave the same results. At room temperature, the reactions were conducted in NMR-tubes.  $^{31}\text{P}$ -NMR spectra were recorded after 2 h. After this time, the degree of conversion was approximately the same as at 80 °C during 25 min.

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### ВПЛИВ СОНЯЧНОЇ ЕНЕРГІЇ НА САМООРГАНІЗАЦІЮ МОЛЕКУЛ ВОДИ. ДОБОВІ, РІЧНІ ТА 11-РІЧНІ ВАРІАЦІЇ

Сонячна енергія сильно впливає на здатність молекул води до самоорганізації. Це виявляється в хімічній активності водних кластерів. Швидкість гідролітичних процесів за участі водних кластерів може змінюватися в дуже широких межах протягом хвилин, годин, днів, місяців та років. Результати регулярних 4-річних (2015–2018) досліджень гідролізу триетилфосфіту вказують на те, що швидкість цієї реакції за всіх однакових умов має добові і річні варіації, а також модулюється 11-річними циклами сонячної активності. Гідролітичний розрив фосфор-кисневого зв'язку в триетилфосфіті можна розглядати як спрощену модельну систему для перетворення аденозинтрифосфату (АТФ) в аденозиндифосфат (АДФ), який, як відомо, лежить в основі біоенергетичних процесів у живих організмах. Залежність біохімічних процесів від сонячної активності внаслідок обертання Землі навколо своєї осі та навколо Сонця добре відома у всіх формах життя (рослинах, тваринах, грибах та бактеріях) як циркадні та циркануальні ритми. Наприклад, внаслідок 11-річних циклів сонячної активності річні кільця в стовбурах дерев мають різну товщину та упорядковані в 11-річні послідовності. Беручи до уваги те, що вода є необхідною складовою частиною у всіх формах життя, можна припустити, що знайдені добові та річні варіації активності води можуть лежати в основі циркадних та циркануальних ритмів.

**Ключові слова:** сонячна енергія, гідроліз, водні кластери, циркадні ритми, циркануальні ритми, 11-річні цикли.

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### ВЛИЯНИЕ СОЛНЕЧНОЙ ЭНЕРГИИ НА САМООРГАНИЗАЦИЮ МОЛЕКУЛ ВОДЫ. СУТОЧНЫЕ, ГОДИЧНЫЕ И 11-ЛЕТНИЕ ВАРИАЦИИ

Солнечная энергия оказывает сильное влияние на способность молекул воды к самоорганизации. Это проявляется в химической активности водных кластеров. Скорость гидролитических процессов с участием водных кластеров может изменяться в очень широких пределах в течение минут, часов, дней, месяцев и лет. Результаты регулярных 4-летних (2015–2018) исследований гидролиза триэтилфосфита указывают на то, что скорость этой реакции при всех одинаковых условиях имеет суточные и годовые вариации, а также модулируется 11-летними циклами солнечной активности. Гидролитический разрыв фосфор-кислородной связи в триэтилфосфите можно рассматривать как упрощённую модельную систему для превращения аденозинтрифосфата (АТФ) в аденозиндифосфат (АДФ), который, как известно, лежит в основе биоэнергетических процессов в живых организмах. Зависимость биохимических процессов от солнечной активности вследствие вращения Земли вокруг своей оси и вокруг Солнца хорошо известна во всех формах жизни (растениях, животных, грибах и бактериях) как циркадные и циркануальные ритмы. Например, вследствие 11-летних циклов солнечной активности годовые кольца в стволах деревьев имеют разную толщину и упорядочены в 11-летние последовательности. Принимая во внимание то, что вода является необходимой составной частью во всех формах жизни, можно предположить, что обнаруженные суточные и годовые вариации активности воды могут лежать в основе циркадных и циркануальных ритмов.

**Ключевые слова:** солнечная энергия, гидролиз, водные кластеры, циркадные ритмы, циркануальные ритмы, 11-летние циклы.