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# Influence of solar activity on water clusters. Annual variations 2015—2019

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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 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. The 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, very large annual variations, and is also modulated by the 11-year cycles of solar activity. Since water is a necessary constituent in all forms of life, the discovered diurnal and annual variations of water clusters' reactivity may underlie the biological circadian and circannual rhythms. The results obtained also point to the fact that the chemical reactivity of water clusters depends on the geographic latitude, and, in summer and winter, it can be significantly different at the same time in the Northern and Southern hemispheres. At the equator, where there should be no seasonal differences, measurements of the rate of triethylphosphite hydrolysis may become an independent method for assessing the solar activity.*

***Keywords:*** *solar activity, solar cycles, hydrolysis, water clusters, circadian rhythms.*

Water possesses unique properties owing to the ability of its molecules to form hydrogen bonds with one another. 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 $(H_2O)_n$ rather than single water molecules. The size of clusters may vary from a few water molecules to several hundreds of them [3]. In large clusters, hydroxyl groups (—OH) are involved in the network of hydrogen bonds, whereas small clusters, especially those of the size $n < 6$, contain a lot of free —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 reactivities, and the rates 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 wa-

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ter in acetonitrile can vary within a very wide range in the course of hours, days, months, and years. It is possible to detect this influence experimentally and to determine the chemical reactivity of water clusters quantitatively by means of the hydrolysis of phosphoric acid esters, for example, triethylphosphite **1** (Fig. 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.

Regular measurements of the rate of hydrolysis of triethylphosphite in acetonitrile (see Fig. 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 invariable, the rate of this reaction is highly dynamic and varies throughout the year over a very wide range (Fig. 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.

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 the low temperature was more significant. For example, in July, the reaction was completed in 10—15 min, 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.

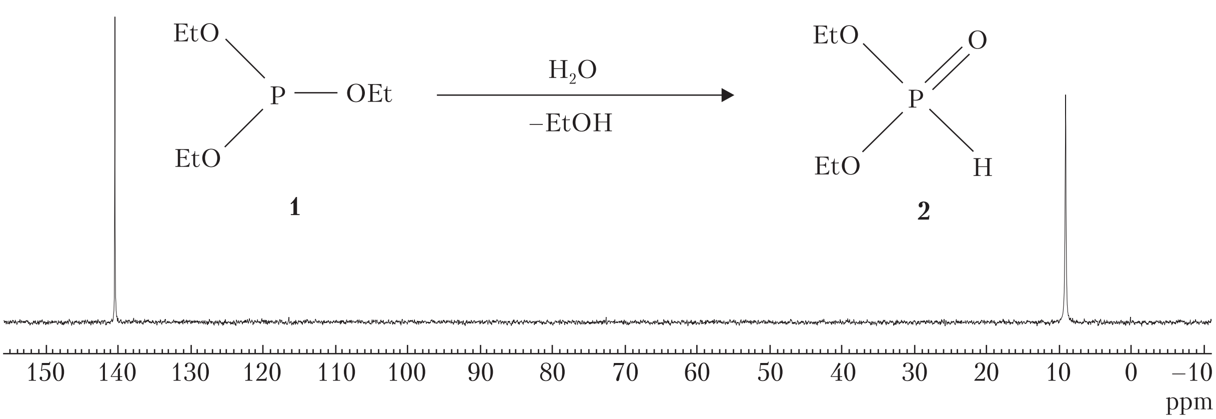


***Fig. 1.*** Hydrolysis of triethylphosphite **1** into diethylphosphonate **2**. $^{31}$P-NMR spectrum displays two signals at +140 ppm and +9 ppm, respectively. Measuring the integral intensities of these signals allows determining the conversion rate

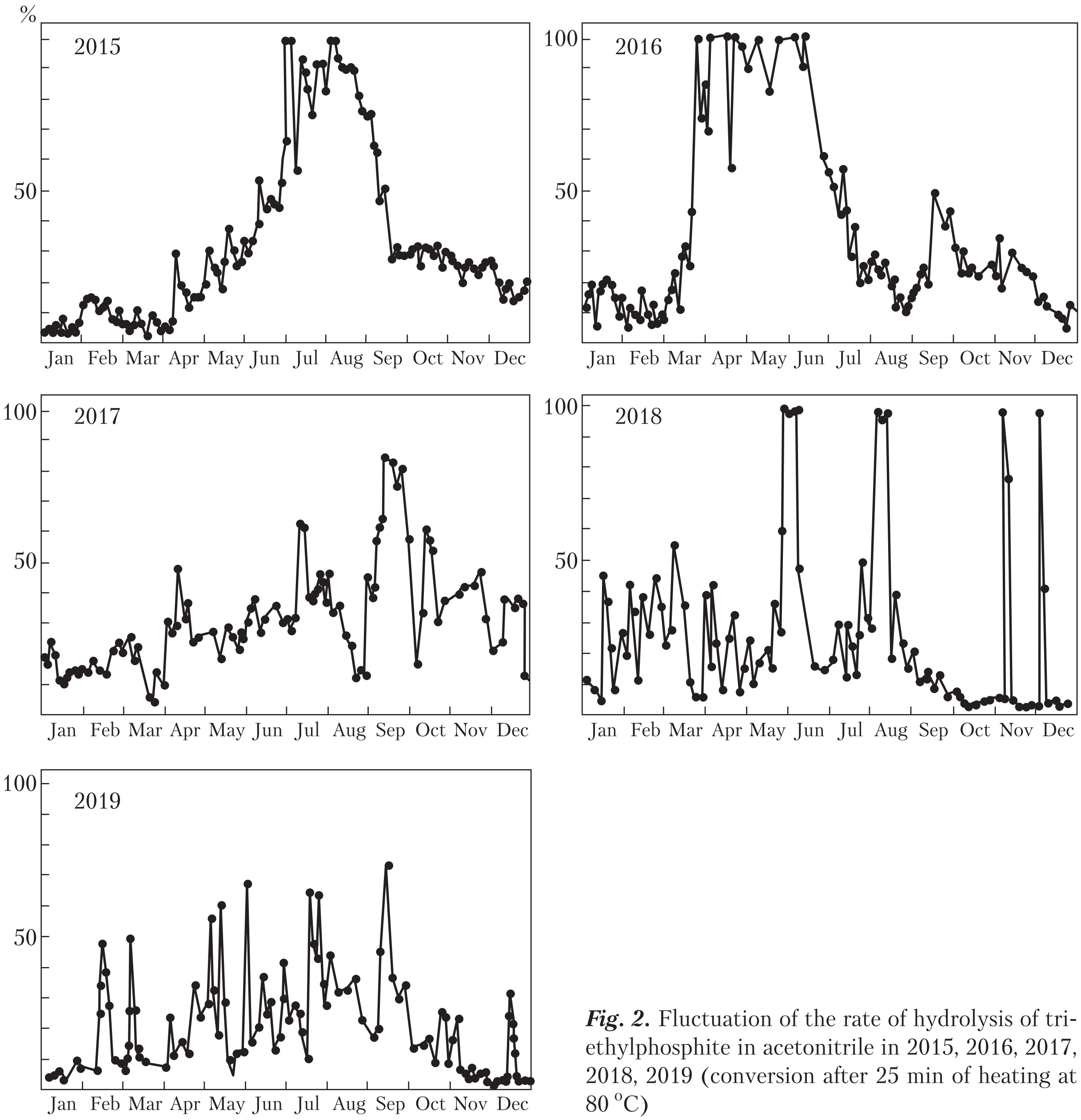


***Fig. 2.*** Fluctuation of the rate of hydrolysis of triethylphosphite in acetonitrile in 2015, 2016, 2017, 2018, 2019 (conversion after 25 min of heating at 80 °C)

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 the 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 the 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 the 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 (see Fig. 2). 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.

In 2017, a noticeable lowering of the 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 (see Fig. 2). That year, another interesting evidence of the influence of solar energy on water clusters was experimentally observed. On August 21, the solar eclipse took place, immediately after which the rate of hydrolysis of triethylphosphite decreased sharply. The 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 up to the previous level.

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. In November and December, the reaction rate became unprecedentedly low. Against the background of low rate, extremely sharp accelerations of 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 coronal mass ejection.

In September 2018, studies were simultaneously conducted in Stuttgart, 1500 km away from Kyiv. In both places, the diurnal deviations were distinctly observed. The average rate in Stuttgart was constantly approximately 2 times higher than in Kyiv. These results indirectly confirm the extraterrestrial influence on the rate of this reaction and exclude a possible influence of any local factors.

In 2019, a further decrease in the rate of hydrolysis was observed (see Fig. 2). In January, the strong deceleration which started in November 2018 continued. Then the rate increased and, as in the previous years, was very dynamic. Very strong sharp accelerations observed in the previous year 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 that took place in December.

Thus, regular measurements over 5 years (from January 2015 till 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 Fig. 2, the picture of annual rate changes is different every year. Moreover, from 2015 till 2020, a general 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.

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 till 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, the 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 the 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 absorbed by the atmosphere of the Earth. For the same reason, the particles of the solar wind cannot reach the surface of the planet either. But they are known to be able to produce secondary active particles in the upper atmosphere — muons, which do not only reach the surface of the Earth, but can penetrate under the ground. The intensity of the muon flow is not stable. It is modulated by solar activity and displays the same annual and diurnal variations as the rate of hydrolysis of triethylphosphite because of the rotation of the Earth around the Sun and its own axis. In summer, the flow of muons is greater than in winter, and, during the day, it reaches its maximum at noon, when the Sun is at its zenith. The confirmation of the fact that muons destroy water clusters and thus accelerate hydrolytic processes was obtained by conducting experiments underground, where this effect should either disappear or slow down significantly. At the depth of 105 m, triethylphosphite was hydrolyzed about 4 times slower than in the building of the Institute and 8—10 times slower than outside of it. It is important to note that the diurnal variations in the rate of hydrolysis underground were exactly the same as on the surface.

The hydrolytic cleavage of phosphorus-oxygen bonds 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 thicknesses 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-h 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 discovered diurnal and annual variations of the reactivity of water clusters may underlie the circadian and circannual rhythms.

**Conclusions.** Thus, the self-organization of water molecules, the stability of water clusters, and their chemical reactivity are extremely sensitive to the extraterrestrial influence associated with the variations of solar activity. This influence obviously has a complex mediated mechanism.

The significant annual change in the chemical reactivity of water clusters due to 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 distributions of solar energy on them. Therefore, measurements of the rate of this reaction in different places can provide important information about the influence of the space weather on the Earth. At the equator, where there should be no seasonal differences, such measurements may become an independent method for assessing solar activity.

**Materials and 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 δ $^{31}$P chemical shifts are referenced to 85 % aqueous $H_3PO_4$.

In a 20 ml glass vial (27 mm in diameter) protected from light water (7 mg) was added to acetonitrile (400 mg). In 5 min, triethylphosphite (30 mg) was added under nitrogen, the vial was sealed and placed on a hotplate. After 25 min 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 of 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.

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ВПЛИВ СОНЯЧНОЇ АКТИВНОСТІ НА ВОДЯНІ КЛАСТЕРИ.
РІЧНІ ВАРІАЦІЇ 2015—2019

Варіації сонячної активності і розподіл сонячної енергії внаслідок обертання Землі навколо своєї осі та навколо Сонця сильно впливають на водяні кластери, внаслідок чого їх хімічна активність у гідролітичних процесах може змінюватися в дуже великому діапазоні. Це явище добре проявляється в гідролізі ефірів фосфористої кислоти. Результати 5-річних регулярних досліджень (2015—2019) гідролізу триетилфосфіту в ацетонітрилі показують, що швидкість цієї реакції за усіх інших рівних умов виявляє добові, дуже великі річні варіації, а також модулюється 11-річними циклами сонячної активності. Оскільки вода є необхідною складовою в усіх формах життя, виявлені добові та річні варіації гідролітичної активності водяних кластерів можуть лежати в основі біологічних циркадних та циркануальних ритмів. Отримані результати також вказують на те, що швидкість цієї реакції залежить від географічної широти, тому влітку та взимку вона може значно відрізнятися водночас у Північній та Південній півкулях Землі. На екваторі, де не повинно бути сезонних відмінностей, вимірювання швидкості цієї реакції можуть стати незалежним методом оцінки сонячної активності.

***Ключові слова:*** *сонячна активність, сонячні цикли, гідроліз, водяні кластери, циркадні ритми.*