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Influence of geoelectric field on chemical reactions on Earth

(Presented by Academician of the NAS of Ukraine V.P. Kukhar)

The existing understanding of chemical thermodynamics presupposes that at the same temperature and other conditions being equal, the rate of a chemical reaction will always and everywhere on Earth be constant. We have found that geoelectric field generated by the Earth's ionosphere, is capable of exerting a strong influence on the rate of chemical processes. Because of the revolution of the Earth around the Sun and varying intensity of the solar irradiance the geoelectric field is highly dynamic and causes the rate of some chemical reactions on the Earth to vary over wide ranges within a year.

Keywords: chemical kinetics, thermodynamics, solar activity, ionosphere, electric field.

The existence of life on the Earth is only possible thanks to the energy which our planet receives from the Sun. This energy consists of a wide spectrum of electromagnetic waves – from infrared to x-rays. The Earth's atmosphere is penetrable for the infrared and visible part of solar rays. Their energy is of fundamental importance for the life on Earth. However, the Earth's atmosphere is not transparent for Extreme Ultraviolet (EUV) and x-ray solar radiation. These rays lose energy in the upper atmosphere above 80 km in collisions with nitrogen and oxygen molecules ionizing them. This results in the formation of ionosphere around Earth which is being continually renewed.

The solar energy reaches Earth also in the form of solar wind – a stream of charged particles, mostly electrons and protons, released from the upper atmosphere of the Sun. Because of the interaction of the solar wind with Earth's magnetic field the magnetosphere is formed.

The distribution of charges inside the magnetosphere and underlying ionosphere is highly dynamic and not homogeneous. It creates various regions of fields, plasmas, and currents. Depending on the geographic latitude, the electric field intensity can be substantially different in different places of the Earth. It may reach high values able to influence technological systems. [1–10]. Thus, geoelectric field together with temperature and gravity is a fundamental condition on the Earth, under constant influence of which all forms of life exist. [11].

The amount of energy of EUV-rays and x-rays which form the ionosphere together with the solar wind energy is a significant part of the total energy that the Earth receives from the Sun. It is logical to assume that this energy, like infrared and visible radiation, can also affect chemical processes on the Earth. If geoelectric field can have such an impact, its value should

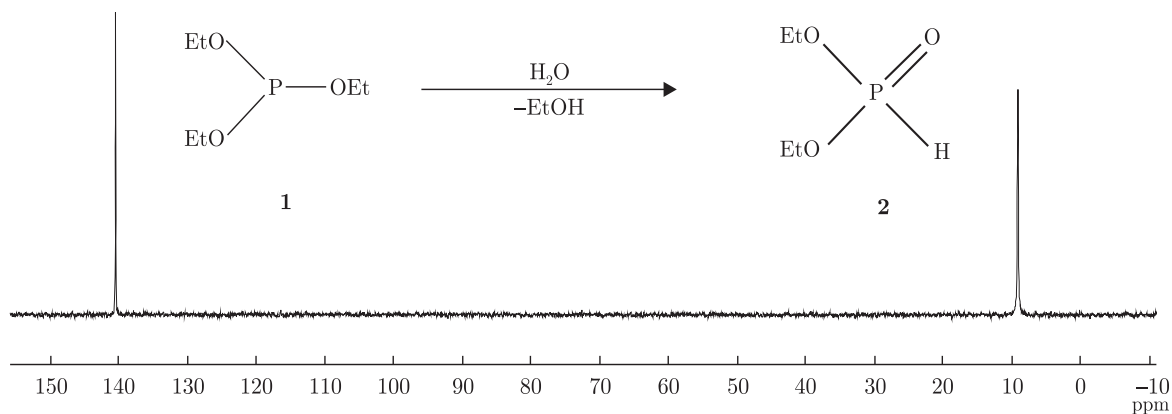


Fig. 1. Hydrolysis of triethyl phosphite **1** into diethyl phosphite **2**. ^{31}P -NMR spectrum displays two signals at +140 ppm and +9 ppm, respectively. Measuring the integral intensities of these signals allows determining the conversion rate

manifest the same seasonal fluctuations over the course of one year as the degree of ionization of the ionosphere at the given latitude. Therefore, the very detection of the dependence of the chemical reaction rate on the position of Earth with respect to the Sun can be absolute proof of the existence of such an effect.

For the experimental verification of this hypothesis hydrolytic cleavage of phosphorus-oxygen bond was chosen. The cleavage of this bond during the conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) is known to underlie bioenergetic processes in living organisms [12, 13].

As a simplified model system hydrolytic cleavage of the P-O bond in triethyl phosphite has been examined in this study. In this reaction, three-coordinated phosphorus atom increases its coordination from 3 to 4, so the reaction product is well distinguishable from the starting compound in the nuclear magnetic resonance (NMR) spectra, which allows measuring the kinetics of the process quickly and reliably (Fig. 1).

Since November 2014, over 1000 experiments have been conducted in different conditions. The experimental data suggest the following conclusions.

The rate of this reaction *ceteris paribus* depends strongly on the position of the Earth with respect to the Sun and therefore shows pronounced seasonal fluctuations. With the growth of the duration of daylight and increase of the impact angle of the solar radiation with respect to the atmosphere over the place of the study an increase in the rate up to the maximum summer values was observed. At the northern latitude $50^{\circ}25'$, where these studies were carried out, the difference between the average values of the “summer” and “winter” rates in 2015 reached 8–10 times (Fig. 2).

The growth of the rate did not take place smoothly. In January the reaction was very slow and accelerated twofold in February. In March it slowed down again. Then, in April it started to grow gradually till the middle of June. After summer solstice a sharp rise occurred (approximately 3-fold), after which the high summer 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. In September, after autumnal equinox till the end of the year the reaction rate declined gradually 2 times more.

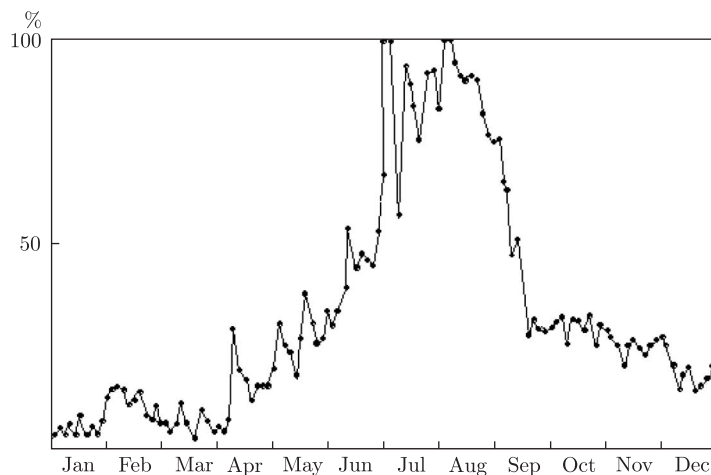


Fig. 2. Fluctuation of the rate of hydrolysis of triethyl phosphite in the course of the year 2015 (conversion after 25 minutes of heating at 80 °C)

It is remarkable that in January 2016 the average rate did not return to the level of the previous year and exceeded it about 2–3 times.

The seasonal dependence observed means that at the same time in summer or winter the rate of this reaction in the northern and southern hemispheres will be substantially different, and this difference should increase, the closer to the poles the reaction is conducted.

One more important conclusion is that this reaction is very sensitive to changes in the ionosphere. Its rate, similarly to the state of the ionosphere, is in constant dynamics and demonstrates not only seasonal, but also more short-term changes, even within one day. In view of these short-term changes, the reaction rate difference between the individual experiments may significantly exceed the average annual difference. For example, on March 20 2015 during spring equinox a slowdown of this reaction was observed and the degree of conversion was about 50 times slower than on July 2.

If the observed dependence of the rate of this reaction on the position of the Earth with respect to the Sun is accounted for by the influence of the geoelectric field, it is logical to assume that the artificial change of the electric field intensity in the volume of the reaction solution should also have an impact on the reaction rate.

Indeed, the shielding of the reaction solution by placing it in a metal grounded box (Faraday cage) reduced the rate of hydrolysis compared with the unshielded sample. Moreover, even on different floors of a building the rates may be different. These measurements were conducted at different times of the year and showed that the effect of shielding diminishes as the reaction rate increases.

A change of the geoelectric field intensity in the reaction solution can be achieved not only by shielding, but also by application of an artificial electric field. For this purpose the field with the intensity of 5 kV/cm was used in this study. This field also affects the rate of hydrolysis of triethyl phosphite. Moreover, it was found that the magnitude and sign of this effect depend on the direction of the applied electric field in space (with respect to Earth's coordinates). Depending on the field vector direction the reaction rate can either increase or decrease or remain unchanged. Such dependence is in itself a confirmation of the presence of external

geoelectric field. The influence of the artificial field of certain orientation also shows pronounced dependence on the position of the Earth with respect to the Sun.

Thus, not only the rate of hydrolysis of triethyl phosphite, but also the impact of the artificial electric field on it is constantly changing throughout the year. However, in contrast to the rate of hydrolysis of triethyl phosphite, which, as described above, increases towards summer and decreases towards winter, the seasonal dependence of the electric field influence on the rate of hydrolysis is more complicated.

In this study the influence of the electric field (5 kV/cm) with the vector whose positive pole was pointed upwards perpendicular to the Earth's surface was examined in detail. It was established that such field orientation is most sensitive to changes in the ionosphere. The following seasonal differences were found in 2015.

From early November 2014 for almost 4 months to February 20, 2015 this artificial field was steadily slowing down the rate of hydrolysis. The magnitude of this slowdown was constantly changing in the range of 0–150 %, although in some experiments it could reach up to 500 %.

After February 20 the period of deceleration came to the end and a period began when the same field with the same intensity and direction caused a steady acceleration of the reaction. As before, during the slowdown, the acceleration value was not constant and fluctuated within the range of 0–150 %. The acceleration period lasted two months till the end of April.

In May, after two months' acceleration, more and more often the absence of any impact was observed and switches to slowdown began to manifest themselves. Thus, gradually, towards the end of May a transition to a new period took place, which lasted until the end of August. The same electric field during this period could both accelerate and decelerate this reaction. Deceleration and acceleration could replace each other every day or last for several days. Attention was also drawn by the fact that in July and August, when the reaction rate reached the summer maximum, the influence of the applied electric field became insignificant and varied in the interval of 0–20 %.

In early September, the impact of the artificial electric field again switched to acceleration. This period lasted throughout September and was similar to the spring acceleration.

In October the accelerating influence of the artificial electric field became insignificant and the absence of any impact was either observed more often or an insignificant slowdown took place. Thus, slowly like in May, transition to the next phase was taking place.

In early November, just like the year before, the influence of an artificial electric field of the given strength and direction, became retarding again. And like the year before this period lasted 4 months.

Graphically the seasonal dependence of the influence of the artificial electric field on the interaction of water with triethyl phosphite in 2015 is presented in Fig. 3.

The fact that both in 2014 and in 2015 the period of sustained slowdown of the reaction by the artificial electric field of given orientation began in November and lasted four months the same time, allows to suppose that the phase change order presented in Fig. 3 and the reaction rate fluctuation shown in Fig. 2 would be repeated with every next revolution of Earth around the Sun. Whether these seasonal changes are influenced by the 11-year solar activity cycle will be established after further lengthy investigations.

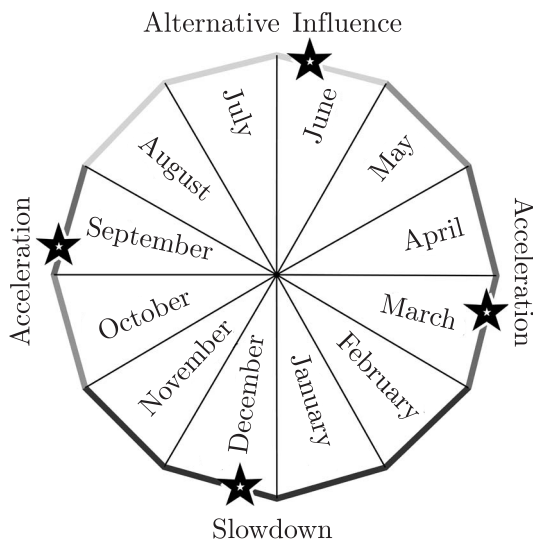


Fig. 3. Change of the influence of the artificial electric field (5 kV/cm, positive pole pointed upwards perpendicular to the Earth's surface) on the rate of hydrolysis of triethyl phosphite over the course of the year 2015. The winter and summer solstice and the vernal and autumnal equinox are indicated by asterisks

The fact that processes inside the magnetosphere and ionosphere can affect even technological systems suggests that the intensity of the geoelectric field can vary within wide limits. The same conclusion may be drawn from the results of this study. In winter 2015 the artificial electric field of 5 kV/cm could change the reaction rate up to 6 times. In summer 2015, when the reaction rate reached its maximum, the impact of this field became negligible. From this we can conclude that the geoelectric field intensity can reach such high values, the change of which by 5 kV/cm is too small to cause a noticeable effect. This fact should be taken into account when studying the influence of an artificial electric field on chemical reactions [14].

Significant variation of the rate of hydrolysis of triethyl phosphite found in this study seems to contradict chemical thermodynamics. However, everything becomes explicable if one takes into account that water molecules exist in the equilibrium with molecular clusters. Electric field can influence the position of this equilibrium which results in accelerating or decelerating the reaction.

Discussion. The phenomenon discovered expands the boundaries of research in different fields of science and raises interesting questions. For example, if the artificial electric field of the same direction and intensity can both accelerate and decelerate the reaction at different times, does it mean that the geoelectric field can change the sign of its charge with respect to the Earth's surface over the place of study? Conducting regular and coordinated measurements of the rate of hydrolysis of triethyl phosphite in different places of the world at different latitudes in the southern and northern hemispheres might help to identify some regularities in the distribution of charges in the ionosphere. In addition, such measurements may help in predicting not only space weather but in determining solar activity as well. It will be interesting to find out how this method will correlate with other already existing methods. [15] The advantage of this one is the possibility to carry out measurements easily and reliably on the Earth's surface, in any scientific center, which is equipped with a NMR spectrometer.

Materials and Methods. All operations were performed under nitrogen. Triethyl phosphite, acetonitrile and water were distilled before use. The ^{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 (diameter 27 mm) triethyl phosphite (40 mg) was added to acetonitrile (390 mg), containing 1.7 % of water. The vial was sealed and placed between two horizontal aluminum plates, whose size was 12×18 cm and the distance between them was 6 cm. The lower plate was heated on a hotplate to 80°C and connected to the negative terminal of a 30 kV voltage. The upper plate was connected to the positive potential. The heating time was dependent on the reaction rate and ranged from 4 to 90 minutes. The vial was then quickly cooled to 0°C , the reaction mixture was transferred to a 5mm-NMR tube and the ^{31}P -NMR spectrum was recorded. The conversion was determined by the integral intensities of the signals of triethyl phosphite (chemical shift 140 ppm) and diethyl phosphite (9 ppm). First, the experiment was performed without the electric field and then in the same vial with the field switched on. After exposure to the electric field the vial was kept at room temperature before the next use for at least 10 days.

The change of the reaction rate in 2015 (without influence of the artificial electric field) is given below in numerical values (Date / Conversion % (Time of heating in minutes)).

January: 05/11%(90m); 07/18%(90m); 12/12%(90m); 13/22%(90m); 16/14%(90m); 18/28%(90m); 22/15%(90m); 27/18%(90m); 30/19%(90m).

February: 02/25%(50m); 09/54%(90m); 10/58%(90m); 11/54%(90m); 12/36%(90m); 16/38%(90m); 18/48%(90m); 20/20%(90m); 23/10%(90m); 24/16%(90m); 25/28%(90m); 26/28%(90m).

March: 02/23%(90m); 03/22%(90m); 04/13%(90m); 06/21%(90m); 16/34%(90m); 17/22%(90m); 20/75%(90m); 23/34%(120m); 24/25%(90m); 26/8%(90m).

April: 06/16%(90m); 12/14%(40m); 22/12%(40m); 24/51%(40m); 27/34%(40m); 29/30%(40m); 30/18%(40m).

May: 06/50%(60m); 08/58%(45m); 14/62%(60m); 15/44%(50m); 21/35%(60m); 25/65%(60m); 26/77%(50m); 27/60%(50m); 28/43%(40m); 29/44%(40m).

June: 02/63%(50m); 03/42%(40m); 04/52%(40m); 05/50%(40m); 06/62%(40m); 09/65%(40m); 10/63%(40m); 16/60%(40m); 17/89%(40m); 18/61%(40m); 19/69%(40m); 22/50%(40m); 23/63%(40m); 24/65%(40m); 25/63%(40m); 26/64%(40m); 18/61%(40m); 30/82%(40m).

July: 03/85%(20m); 06/66%(15m); 07/33%(30m); 08/50%(30m); 09/62%(30m); 10/46%(30m); 13/82%(30m); 15/86%(30m); 16/73%(20m); 20/57%(20m); 21/55%(20m); 22/68%(20m); 23/65%(20m); 24/79%(22m); 27/90%(30m); 28/74%(30m); 29/73%(20m); 30/76%(25m); 31/74%(20m).

August: 03/63%(20m); 04/84%(20m); 10/82%(20m); 11/74%(20m); 12/71%(20m); 13/81%(20m); 14/69%(20m); 17/67%(20m); 18/71%(20m); 20/45%(20m); 21/51%(20m); 25/65%(20m); 26/62%(20m); 27/65%(20m); 28/64%(20m); 31/60%(20m).

September: 01/60%(20m); 02/65%(20m); 03/68%(20m); 04/59%(20m); 07/69%(20m); 11/27%(20m); 11/21%(20m); 14/27%(30m); 15/50%(60m); 16/70%(60m); 17/64%(60m);

18/48%(40m); 21/48%(40m); 22/57%(40m); 23/64%(40m); 24/58%(40m); 25/45%(40m); 28/45%(40m); 29/47%(40m); 30/46%(40m).

October: 01/41%(40m); 02/44%(40m); 06/51%(40m); 09/55%(50m); 12/50%(50m); 13/44%(50m); 15/57%(60m); 16/47%(60m); 19/61%(60m); 20/50%(60m); 21/51%(60m); 26/57%(60m); 28/40%(945m); 29/49%(45m); 30/48%(45m).

November: 02/54%(45m); 03/57%(45m); 04/55%(45m); 05/55%(45m); 06/43%(45m); 09/51%(45m); 10/30%(45m); 11/55%(50m); 13/45%(45m); 16/47%(45m); 17/34%(45m); 18/46%(45m); 19/53%(45m); 20/51%(45m); 23/51%(45m); 26/49%(45m); 30/58%(60m).

December: 01/50%(45m); 02/49%(45m); 03/56%(45m); 09/33%(45m); 11/45%(45m); 16/27%(45m); 21/48%(45m); 23/35%(45m); 24/47%(50m); 25/35%(60m); 28/59%(71m).

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Влияние геоэлектрического поля на химические реакции на Земле

Существующее представление о химической термодинамике предполагает, что при одинаковой температуре и прочих равных условиях скорость химической реакции всегда и везде на Земле является постоянной. Автором обнаружено, что геоэлектрическое поле, генерируемое ионосферой Земли, способно оказывать сильное влияние на скорость химических процессов. Вследствие вращения Земли вокруг Солнца и изменяющейся

интенсивности солнечного излучения геоэлектрическое поле чрезвычайно динамично и способно вызывать изменение скорости некоторых химических реакций на Земле в больших пределах в течение года.

Ключевые слова: химическая кинетика, термодинамика, солнечная активность, ионосфера, электрическое поле.

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Вплив геоелектричного поля на хімічні реакції на Землі

Існуюче уявлення про хімічну термодинаміку передбачає, що при однаковій температурі та інших рівних умовах швидкість хімічної реакції завжди і повсюди на Землі буде однаковою. Автором встановлено, що геоелектричне поле, що генерується іоносферою Землі, спроможне сильно впливати на швидкість хімічних процесів. Внаслідок обертання Землі навколо Сонця та інтенсивності сонячного випромінювання, що змінюється, геоелектричне поле дуже динамічне та спроможне викликати зміну швидкості деяких хімічних реакцій в широких межах впродовж року.

Ключові слова: хімічна кінетика, термодинаміка, сонячна активність, іоносфера, електричне поле.