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Ethylene: the laws of chemistry have not yet been canceled

B.A. Kurchii

IEC, 9, Gagarina Str., Irpin, 08200, Ukraine

Summary. The aim of this report is to present the mechanisms of ethylene functioning in the living systems on the bases of fundamental laws of chemical reactions. A point of view herein described is based on the free radical mechanism of ethylene action.

Keywords: ethylene, free radicals, receptors, gene key, gene lock.

The mountain labored and brought forth a mouse: Paradox in the ethylene studies

The gaseous substance ethylene (ET, the smallest substance among plant growth regulators) is the most known as regulator of growth and development of plants. Ethylene also plays an important role in plant responses to abiotic and biotic factors [1, 14].

For decades many intricate hypotheses to explain the molecular mechanism of ET action have been formulated. Nevertheless, current research data in ET biology is a collection of puzzles. And the research paradox is plain to see: The huge numbers of research publications have been devoted to ET, but the intended goal — deciphering the molecular mechanism of ET action has not been reached. Moreover, publications of last decades suggest: More insights, but more questions. We have a logic brain teaser: Either this is really an insoluble task or researches are carried out in the wrong way. Herein I discuss possible solutions to this paradox and I want to express my point of view on this research problem.

Structure/activity relationships

ET (ethene, C_2H_4, 28 g/mol) at room temperature and atmospheric pressure is a colorless, flammable gas, having a sweet, unpleasant odor and taste. ET is only very slightly soluble in water, but dissolves in nonpolar solvents or in solvents of low polarity [19, 20].

Of the total flow of publications take a look at the next publications. It was found that steric factors play essential role in the biological activity of aliphatic acyclic alkenes. As shown by Burg and Burg [5] ET possessed in the higher biologically activity in comparison to propylene and 1-butene (half maximal responses were in the ratio 1: 130: 140,000), ethane was not biologically active.

Studying the mechanism of ET action in etiolated pea seedlings Beyer [4] detected no apparent differences in the biological activity of tetradeuteroethylene (C_2D_4) and ordinary ET (C_2H_4). No detectable exchanges between the deuterium atoms of C_2D_4 and the hydrogen atoms of the tissue were found, and no conversion had occurred to the corresponding *cis*-$C_2D_2H_2$ or *trans*-$C_2D_2H_2$ isomers.

Chemical properties of ethylene

ET is a stable chemical compound and enters into a small number of reactions. The next reactions have been well studied: halogenation, hydroboration, hydrogenation and hydration reactions, epoxidation reaction with peroxycarboxylic acids, dihydroxylation reaction with potassium permanganate, and reaction with sul-

*** Corresponding author.**
Tel.: +38097-4818848
E-mail address: kurchii@mail.ru

furic acid. These reactions occur under normal conditions (temperature and atmospheric pressure), some other reactions take place in the presence of catalysts at high temperature and air pressure [20].

Metabolism of ethylene in the biological systems

It is found that in living organisms ET has been transformed into ethylene oxide (EO). In the experiment with labeled ET 85-95 % of the ^{14}C appearing in EO in less than 2 h of exposure broad-bean cotyledons with $[^{14}C]C_2H_4$ [12]. Also ET has been transformed into EO in the mice and human tissues [21].

The including of ET into cellular metabolites was demonstrated in the several experiments. So Beyer [3] detected that $^{14}C_2H_4$ was incorporated and metabolized to $^{14}CO_2$ by intact pea seedlings. The radioactive ET possesses in greater mass in comparison to nonradioactive ET, and thus differences in the mass lead to different bond energies, that affect reaction rates (this phenomenon is called a kinetic isotope effect).

No isotope effects were detected in the work of Burg and Burg [5].

No difference has been found between deuterated C_2D_4 (mass 32), C_2D_3H (mass 31), $C_2D_2H_2$ (mass 30) and C_2DH_3 (mass 29) and protonated ET in inhibiting the growth of pea roots. Authors concluded that splitting carbon to hydrogen bonds did not occur during ET action and hence, covalent bonding is not important in ET action [2].

Thus, the absence of isotope effects can suggest the free radical reactions.

Ethylene oxide is a toxic substance to living things

EO causes cytogenetic alterations, mutations and cancer [10, 11].

The egg or the chicken, which one came first?

Current viewpoint on the ET action is focused on the theory of receptors (ETR1, ERS1, ETR2, ERS2, EIN4 in *Arabidopsis thaliana*), which present some complexes of ET, copper and proteins, which have similarities to two-component regulators of bacteria and yeast [13]. Unfortunately, there is no detailed information how these complexes are formed based on the chemical laws.

For instance, in accordance to the basic principles of the Lewis theory [20] an acid is an electron-pair acceptor and a base is an electron-pair donor, and thus $H_2C{=}CH_2$ is π-HOMO Lewis base and heavy metals (hard to soft) are a Lewis acid.

As follows from Lewis theory the reactions between $H_2C{=}CH_2$ and Cu^{2+} (Cu, Cu^+,) yield adducts with one of the following possible bonds (covalent, polar-covalent or back-bond).

Pearson classified Lewis acids and Lewis bases as *hard*, *borderline* or *soft*. Pearson postulated: hard [Lewis] acids prefer to bind to *hard* [Lewis] bases to give an ionic (charge-controlling) complex, and *soft* [Lewis] acids prefer to bind to *soft* [Lewis] bases to give a covalent (frontier molecular orbitals) complex [18]. In accordance to Pearson's classification system Cu^+, Ag^+ and Au^+ are *soft* [Lewis] acids, Cu^{2+} is a *borderline* [Lewis] acid, and C_2H_4 and CO are *soft* [Lewis] bases. Hence, *soft* [Lewis] acids bind to *soft* [Lewis] bases to give frontier molecular orbitals controlled (covalent) complexes. Unfortunately, Pearson's theory says nothing about mixed *hard-soft*, *hard-borderline* and *soft-borderline* complexes.

Thus, such species as CO_2 and Cu^{2+}, that do not contain an atom of hydrogen in their formulas, function as Lewis acids by accepting an electron pair in reactions [19]. The product of any Lewis acid-base reaction is called an adduct, a single substance that contains a new covalent bond, while a hard acid and a hard base tend to form ionic bonds [19, 20]. Also, weak acids and weak bases dissociate into ions very little in aqueous solution, and most of their molecules remain intact [19].

In the presented ethylene-receptor theory [14] copper binds to proteins. In any protein can be present next flanking groups -SH, -N=NH, $-NH_2$, =O, that can form the bond with copper. How this complex than reacts with ET without breaking the covalent bonds nothing is known.

There is next possibility when firstly is formed the complex between ET and copper. In this case the broken of the covalent bond between ET and copper can lead to the transformation of ET into ethane. But ethane is not biologically active [5]. Consequently, this reaction produces the biologically inactive compound.

There is another viewpoint on the nature of the bond between ET and copper. As noted Frenking [8] the weak copper-ethylene bond of $\{Cu(C_2H_4)\}$ suggests that the compound can be considered as van der Waals' complex, where the bonding between the metal and the olefin is mainly due to electrostatic attraction. From this follows that complex ET-copper will not be stable in water solution.

Hence, the question which one came first: Formation the complex ET-receptor and then its action or vice versa remains open.

Copper is a powerful biologically active chemical

Phytotoxic effects of copper have been observed in the experiments with different plants [9, 16]. Also copper is using as an effective fungicide [17]. In animals Cu influences many diseases and disorders [7]. Thus, copper can also cause many biological effects independently of ET.

Ethylene biologists are like being in a dark room and looking for a black cat

Why look for ET receptors when mechanism of their action cannot be explained by fundamental chemical reactions. Ethylene at normal temperature and atmospheric pressure can easily react only with free radical agents [6, 9, 20]. Hence, the molecular mechanism of ethylene action *in vivo* is possible in the free radical state [15]:

In free radical state ET can initiate free radi-

$$CH_2{=}CH_2 + \dot{R} \longrightarrow \dot{C}H_2{-}CH_2{-}R \longrightarrow \text{ACTION}$$

cal chain reactions of lipids and other cellular biopolymer oxidation and also conjugates with any cellular substances. Several conjugates of ethylene with proteins can be recognized as ethylene-receptors complexes. This is the consequence of ethylene action *in vivo*, but not the cause of its biological activity.

Conclusions

In this report I presented the view point on mechanism of ET action that is based on the idea of free radical (or ROS) mechanisms of ET action in the biological systems. ET action at the genetic level is performed with the participation of the gene keys composed from DNA. It should be noted that a significant factor that determines the growth and development of living systems is a balance between free radicals and antioxidants.

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Б.О. Курчій

ІЕК, вул. Гагаріна, 9, м. Ірпінь, Київська область, 08200, Україна

Резюме. Метою цієї статті є представлення механізмів функціонування етилену в живих системах, ґрунтуючись на фундаментальних законах хімічних реакцій. Представлена точка зору базується на вільнорадикальних механізмах дії етилену.

Ключові слова: етилен, вільні радикали, рецептори, генний ключ, генний замок.

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